

NOAA Technical Memorandum NMFS-SEFC-42



NOAA/NMFS ANNUAL REPORT TO EPA

Environmental Assessment of Buccaneer Gas and Oil Field in the Northwestern Gulf of Mexico, 1978 - 1979

A report to the Environmental Protection Agency on work conducted
under provisions of Interagency Agreement EPA-IAG-D5-E693-E0
during 1978 - 1979.

Volume VIII TRACE METALS

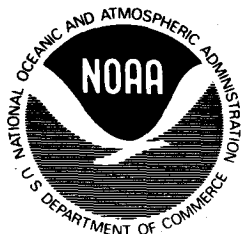


SOUTHEAST FISHERIES CENTER GALVESTON LABORATORY



GALVESTON, TEXAS
NOVEMBER 1980

U.S. DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration
National Marine Fisheries Service
Southeast Fisheries Center
Galveston Laboratory
Galveston, Texas 77550



NOAA Technical Memorandum NMFS-SEFC- 42

Environmental Assessment of Buccaneer Gas and Oil Field In the Northwestern Gulf of Mexico, 1978-1979

VOL. VIII - TRACE METALS

BY

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**A report to the Environmental Protection Agency on work conducted under
provisions of Interagency Agreement EPA-IAG-D5-E693-EO during 1978-1979.**

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This volume should be cited as follows:

Tillery, J. B. 1980. Trace metals. Vol. VIII. In: Jackson, W. B. and E. P. Wilkens, (eds.). Environmental assessment of Buccaneer gas and oil field in the northwestern Gulf of Mexico, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-42, 93 p. Available from: NTIS, Springfield, Virginia.

Volume VIII - TRACE METALS

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LIST OF VOLUMES

This Annual Report is printed in ten separate volumes:

Volume I - SYNOPSIS/DATA MANAGEMENT

Work Unit 2.6.1 Synopsis

NMFS/SEFC Galveston Laboratory

Principal Investigators

Work Unit 2.2.3 Implement, Monitor, and Modify Data Management System

NMFS/SEFC National Fisheries Engineering Laboratory

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Volume II - SEDIMENTS AND PARTICULATES

Work Unit 2.3.2 Investigations of Surficial Sediments and Suspended Particulates at Buccaneer Field

Texas A&M University

J. Brooks, Ph.D.

E. Estes, Ph.D.

W. Huang, Ph.D.

Volume III - FISHES AND MACROCRUSTACEANS

Work Unit 2.3.5 Effect of Gas and Oil Field Structures and Effluents on Pelagic and Reef Fishes, Demersal Fishes, and Macrocrustaceans

LGL Ecological Research Associates, Inc.

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Volume IV - BACTERIA

Work Unit 2.3.7 Bacterial Communities

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Volume V - FOULING COMMUNITY

Work Unit 2.3.8 Effects of Gas and Oil Field Structures
and Effluents on Fouling Community
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Volume VI - CURRENTS AND HYDROGRAPHY

Work Unit 2.3.9 Currents and Hydrography of the Buccaneer
Field and Adjacent Waters

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Corporation

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Volume VII - HYDROCARBONS

Work Unit 2.4.1 Hydrocarbons, Biocides, and Sulfur

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Volume VIII - TRACE METALS

Work Unit 2.4.2 Trace Metals

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Volume IX - FATE AND EFFECTS MODELING

Work Unit 2.5.1 Sources, Fate and Effects Modeling

Science Applications, Inc.

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Volume X - HYDRODYNAMIC MODELING

Work Unit 2.5.2 Hydrodynamic Modeling

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GUIDE TO USERS OF THE ANNUAL REPORT

Volume I (SYNOPSIS/DATA MANAGEMENT) of the Annual Report is designed to be used as a briefing document and as a key to more detailed scientific and technical information contained in Volumes II through X. Objectives, methods and results for each work unit are summarized in greatly abbreviated form within Volume I to facilitate dissemination of information. Thus, Volume I can be used alone or as a reference to companion Volumes II through X. Complete citations for literature cited in Volume I can be found in the Volumes II through X in which the detailed work unit reports are presented.

It is hoped that such an approach to environmental impact information dissemination will make the Annual Report a more useful and widely read document.

FOREWORD

Increased petroleum development of the outer continental shelf (OCS) of the United States is anticipated as the U.S. attempts to reduce its dependency on foreign petroleum supplies. To obtain information concerning the environmental consequences of such development, the Federal Government has supported major research efforts on the OCS to document environmental conditions before, during, and after oil and gas exploration, production, and transmission. Among these efforts is the Environmental Assessment of Buccaneer Gas and Oil Field in the Northwestern Gulf of Mexico, a project funded by the Environmental Protection Agency (EPA) through interagency agreement with the National Oceanic and Atmospheric Administration (NOAA) and managed by the National Marine Fisheries Service (NMFS), Southeast Fisheries Center (SEFC), Galveston Laboratory, in Galveston, Texas. Initiated in the autumn of 1975, the study is now in its last year. Its major products have been annual reports disseminated by the National Technical Information Service, data files archived and disseminated by NOAA's Environmental Data and Information Service, and research papers written by participating investigators and published in scientific or technical journals. Results have also been made available through EPA/NOAA/NMFS project reviews and workshops attended by project participants, and various governmental (Federal and State), private, and public user groups. The final products will be milestone reports summarizing the findings of the major investigative components of the study.

Objectives of the project are (1) to identify and document the types and extent of biological, chemical and physical alterations of the marine ecosystem associated with Buccaneer Gas and Oil Field, (2) to determine specific pollutants, their quantity and effects, and (3) to develop the capability to describe and predict fate and effects of Buccaneer Gas and Oil Field contaminants. The project uses historical and new data and includes investigations both in the field and in the laboratory. A brief Pilot Study was conducted in the autumn and winter of 1975-76, followed by an extensive biological/chemical/physical survey in 1976-77 comparing the Buccaneer Gas and Oil Field area with adjacent undeveloped or control areas. In 1977-78, investigations were intensified within Buccaneer Gas and Oil Field, comparing conditions around production platforms, which release various effluents including produced brine, with those around satellite structures (well jackets) which release no effluents. In 1978-79, studies around Buccaneer Gas and Oil Field structures focused on (1) concentrations and effects of pollutants in major components of

the marine ecosystem, including seawater, surficial sediments, suspended particulate matter, fouling community, bacterial community, and fishes and macro-crustaceans, (2) effects of circulation dynamics and hydrography on distribution of pollutants, and (3) mathematical modeling to describe and predict sources, fate and effects of pollutants. The final year, 1979-80, of study is continuing to focus on items (1) and (2) and on preparation of the milestone reports which will represent the final products of this study.

This project has provided a unique opportunity for a multi-year investigation of effects of chronic, low-level contamination of a marine ecosystem associated with gas and oil production in a long-established field. In many respects, it represents a pioneering effort. It has been made possible through the cooperation of government agencies, Shell Oil Company (which owns and operates the field) and various contractors including universities and private companies. It is anticipated that the results of this project will impact in a significant way on future decisions regarding operations of gas and oil fields on the OCS.

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INTRODUCTION

Location of Study Area

The area selected for study is the operational Buccaneer Gas and Oil Field located approximately 49.6 kilometers (26.8 nautical miles) south southeast of the Galveston Sea Buoy off Galveston, Texas (Figure 1). This field was selected in 1975 as the study area because: (a) the field had been in production for about 15 years, which time had allowed full development of the associated marine communities; (b) it was isolated from other fields which facilitated the selection of an unaltered area (for comparison) within a reasonable distance of the field; (c) it produced both gas and oil that represented sources of pollutants from marine petroleum extraction; (d) its location simplified logistics and reduced the cost of the research; and (e) the Texas offshore area had not been fully developed for gas and oil production but was expected to experience accelerated exploitation in the future.

Operation History of Buccaneer Field

Buccaneer Field was developed by Shell Oil Company in four offshore blocks leased in 1960 and 1968 as follows:

<u>Year</u>	<u>Lease Number</u>	<u>Block Number</u>	<u>Acreage</u>	<u>Hectares</u>
1960	G0709	288	2,790	1,129
1960	G0713	295	4,770	1,930
1960	G0714	296	4,501	1,821
1968	G1783	289	2,610	1,056

In development of the field, 17 structures were built; two are production platforms, two are quarters platforms, and 13 are satellite structures surrounding well jackets. Initial exploratory drilling began about mid-summer of 1960 with mobile drilling rigs. When (as the result of the exploratory drilling) proper locations for platforms were selected, the permanent production platforms were constructed.

There have been no reports of major oil spills from this field. There have been some reported losses of oil due to occasional mechanical failure of various pieces of equipment. The largest reported spill was three barrels in 1973. The reported oil spill chronology and quantity for Buccaneer Field is as follows:

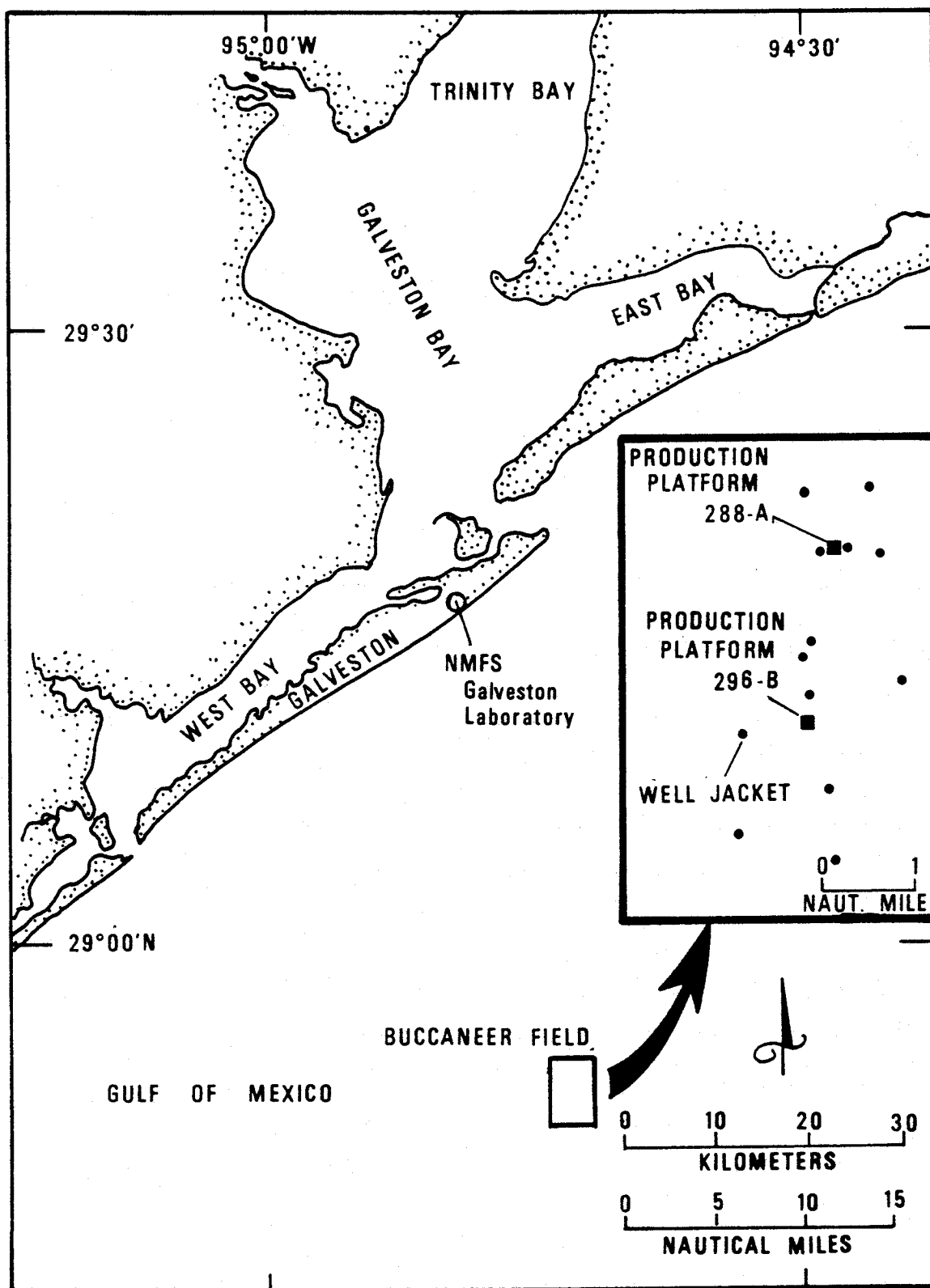


FIGURE 1. LOCATION OF BUCCANEER FIELD

reported spill was three barrels in 1973. The reported oil spill chronology and quantity for Buccaneer Field is as follows:

<u>Date</u>	<u>Source</u>	<u>Amount</u>	
		<u>Barrels</u>	<u>Liters</u>
September 1973	Platform 296-B	0.5	79
November 1973	Unknown	3.0	477
July 1974	Platform 296-B	0.5	79
August 1974	Platform 296-B	1.7	265
September 1975	Platform 288-A	0.2-0.4	38-56
Totals		5.9-6.1	938-956

Buccaneer Field first began operations with the production of oil. Later, when significant quantities of gas were found, the field began producing both oil and gas and has continued to do so to date.

The production platforms and satellites (well jackets) are connected by a number of pipelines with a 50.8 centimeters (20-inch) diameter main pipeline connecting the field to shore. All of the pipelines that are 25.4 centimeters (10 inches) or greater in diameter are buried. The Blue Dolphin Pipeline Company was granted a pipeline permit (No. G1381, Blocks 288 and 296) in 1965 and has operated the pipeline since its construction.

Buccaneer Field occupies a limited area (about 59.3 km²; 22.9 . statute miles) leased in the northwestern Gulf of Mexico. Four pes of structures are located in Buccaneer Field: production platforms, quarters platforms, satellites (well jackets), and flare racks. These are shown in Figure 2, which is an oblique aerial photograph of production platform 288-A and vicinity within Buccaneer field. A map of Buccaneer Field, (Figure 3) depicts the locations of platforms and satellites within the field.

SATELLITE
WELL JACKET

PRODUCTION
PLATFORM

QUARTERS
PLATFORM

FLARE STACK

FIGURE 2. BUCCANEER FIELD STRUCTURES

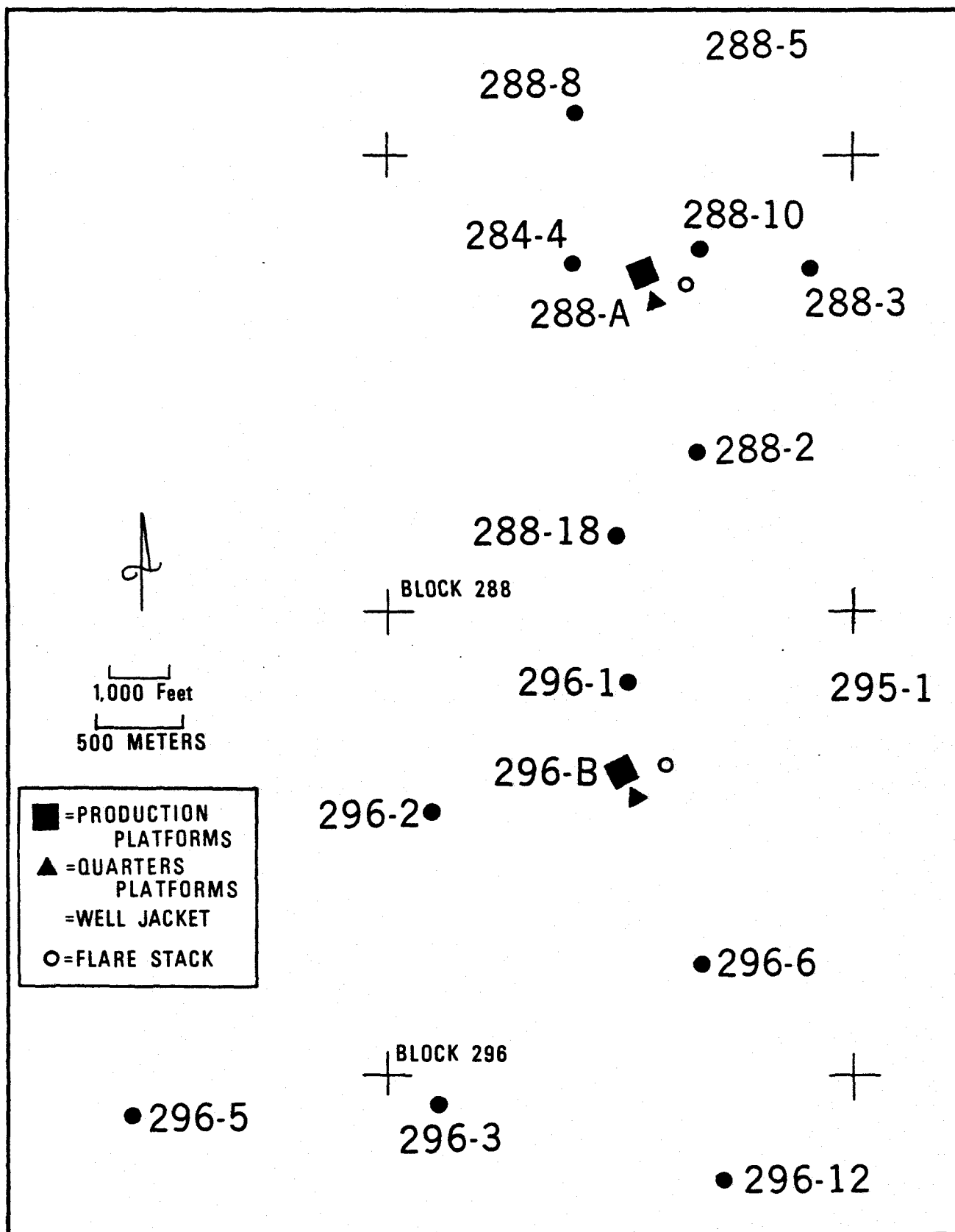


FIGURE 3. SHELL OIL COMPANY'S ALPHANUMERICAL IDENTIFICATION OF
BUCCANEER GAS AND OIL FIELD STRUCTURES

WORK UNIT 2.4.2 - TRACE METALS

Southwest Research Institute

J. B. Tillery

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I. INTRODUCTION

A. Background

The "Environmental Assessment of the Buccaneer Gas and Oilfield in the Northwestern Gulf of Mexico" is a multidisciplinary program started in 1975 to examine what effect development of offshore oil and gas resources have on the marine environment and ecosystems existing on the Outer Continental Shelf (OCS) areas of Texas. This program is jointly sponsored by the Environmental Protection Agency (EPA) and the National Oceanic and Atmospheric Administration (NOAA). The Environmental Research Division of the National Marine Fisheries Service, Southeast Fisheries Center, Galveston Laboratory, have the management responsibilities for this program.

The objectives of this program as described in the "request for proposal" (RFP) are: (1) first year (1975) was a descriptive survey of environmental and ecosystem variables as compared to an adjacent unaltered area; (2) the second year was an intensive study of the environmental and ecosystem variables with the emphasis placed upon the comparison of production platforms (with discharges) with satellite structures (well jackets) having no discharges, and (3) in the third year the sources, fate and effects of oilfield pollutants in major ecosystem components, their mode of transport and bioaccumulation are to be investigated.

Only two other major studies funded by the government have directly investigated the effects of oil and gas drilling/production on the marine environment in the Gulf of Mexico. The 1975-76 Mississippi, Alabama, Florida (MAFLA) Rig Monitoring Study (Alexander et al., 1977) examined the impact of exploratory drilling operations on the marine environment and ecosystems before, during, and after the actual drilling operations. The other study is the 1978 Louisiana platform study (Bedinger et al., to be published

in 1980) which investigated the long-term fate and effect production platforms have on the marine environment and ecosystems operating on the OCS off the Louisiana coast. Both of these studies were funded by the Bureau of Land Management (BLM). These studies were to augment the larger "baseline" studies of the 1976-1977 South Texas Outer Continental Shelf (STOCS) and the 1977-78 baseline monitoring studies, Mississippi, Alabama, Florida Outer Continental Shelf (MAFLA), also sponsored by the BLM.

The Buccaneer Gas and Oilfield Study fulfills a unique position in relation to these other studies in that it provides long-term monitoring of a marine environment exposed to chronic, low level oilfield pollutants in an area free from other major pollutants sources.

B. Purpose

The objective of this investigation was to determine the fate and effect, bioaccumulation and possible sources of 12 heavy metals that are associated with drilling and production activities on the marine environment and marine ecosystem in the Buccaneer gas and oilfield. This was accomplished by determining the concentrations of Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sr, and Zn in (1) surficial sediments, (2) suspended particulate matter, (3) sea water, (4) produced brine, (5) pelagic fish, (6) demersal fish, (7) macrocrustaceans, and (8) bioassay samples collected during four consecutive seasons from the area around two production platform structures (288-A, 296-B), a flare stack at 296-B, and a well jacket (288-5) (Figure 1, page 2.4.2-47).

The Buccaneer gas and oilfield is located approximately 50 km southeast of Galveston (Figure 1). It was developed by Shell Oil Company between 1960 and 1968.

II. METHOD AND MATERIALS

A. Instrumentation

The following atomic absorption spectrophotometers were used for all metal analyses:

a Perkin-Elmer Model 5000 Atomic Absorption Spectrophotometer (AAS) with a HGA-500 Graphite Furnace and multigas flame capability. This system is completely automated and includes a Perkin-Elmer AS-3 Automatic Micro Sampler System for flame analysis and a Perkin-Elmer AS-1 Auto Sampling System for flameless analysis.

a Perkin-Elmer Model 560 Atomic Absorption Spectrophotometer with a HGA-500 Graphite Furnace and multigas flame capability.

a Perkin-Elmer Model 403 AAS with an Instrumentation Laboratory IL-455 Graphite Furnace.

a Perkin-Elmer Model 306 AAS with a HGA-2000 Graphite Furnace.

B. Sample Collection and Analysis

1. Sample Collection

All surficial sediments, sea water, suspended particulates, produced brine, and biota samples for trace metal analyses were collected by other work groups (2.3.2, 2.3.4, 2.3.5, and 2.3.8) following instructions provided by 2.4.2.

Samples were collected using noncontaminating techniques and stored in preacid-washed polyethylene containers provided by Work Group 2.4.2. All samples were refrigerated after collection and were transported to the Galveston laboratory at which time they were frozen. Samples remained frozen until ready for preparation.

2. Surficial Sediments

A "partial" digestion was done on all sediment samples. On 25 percent of the total number of sediment samples, a "total" digestion was performed.

a. Partial Digestion

The sediment subsample was removed from the freezer and allowed to thaw completely and equilibrate with room temperature.

An acid-cleaned glass rod was used to thoroughly mix the wet sediment. Approximately 60-80 grams of the wet sediment was weighed into a tared polyethylene beaker and particles greater than, or equal to, 3 mm were removed with Teflon-coated forceps. The beaker was then covered with a thin sheet of tissue paper and placed in a drying oven (60°C) until sediment reached a constant dry weight. The sample was reweighed to determine water loss. The sample was then ground in a mortar and pestle and stored in an acid-cleaned polyethylene bottle.

A five-gram aliquot of the dried sediment was weighed into a 250-mL polyethylene screw-cap Erlenmeyer flask. Twenty-five milliliters of 5N HNO₃ was added to the sample. The flask was sealed and placed on a mechanical shaker at low speed for two hours. The leachate was quantitatively transferred to a 50-mL polyethylene centrifuge tube using three distilled water rinsings of the Erlenmeyer flask. The sample was then centrifuged at 2500-3000 RPM's for 20 minutes in order to separate the suspended silica material from the leach, thereby preventing an interference in the flame and flameless AAS determination of the analyte metals. The leachate was quantitatively transferred to a 50-mL polyethylene volumetric flask and made to volume with distilled water. This leachate was used for metal analysis. All metals, except Cd, were determined by flame AAS. Hg was determined on a one-gram aliquot of the original sample by cold vapor AAS.

b. Total Digestion

A ten-gram subsample of the dried sediment (as prepared above for "partial" digestion) was sieved through a 100 mesh stainless steel (ATM Corporation, Milwaukee, Wisconsin) screen using an ATM Sonic Sifter. A five-gram subsample of the preground, presieved sample was weighed into a 250-mL Teflon

beaker. Twenty-five mL of concentrated HCl was added to the sample and the beaker was covered with a Teflon watchglass. The sample was placed on a hot plate (90-100°C) for one hour to digest. Following the HCl digestion, the sample was allowed to cool in a clean bench and 15 mL of concentrated HNO₃ was added. The beaker was then returned to the hot plate for 45 minutes of heating (90-100°C). The beaker was removed and allowed to cool before adding 25 mL of 48 percent HF to disrupt the crystalline lattice of the sediment. The sample was returned to the hot plate for a third time and heated for two hours. After this final digestion, the sample was cooled and quantitatively transferred to a 50-mL polyethylene volumetric flask. The beaker was rinsed three times with distilled water and the flask brought to volume with distilled water.

All metals except Cd were determined by flame AAS. Cadmium was determined by flameless AAS. Hg was not to be determined on this total digestate. A nitrous oxide/acetylene flame was used to determine Ba, and Sr.

3. Sea Water and Produced Brine Discharge

a. General

The procedure for trace metal analysis of brines and sea water was an APDC-DDC/CHCl₃ (ammonium pyrrolidine dithiocarbamate-diethyldithiocarbamate/chloroform) extraction followed by a second extraction of the organic phase to stabilize the extracted metals (Jan and Young, 1978; De, et al., 1970). Barium and strontium were determined on the original acidified sample. All metal determinations were made by flame or flameless AAS except Hg for which cold vapor was used.

b. Sea Water/Brine Extraction Procedure

Frozen samples were allowed to thaw to room temperature and the total volume of sample collected determined. The samples

were then acidified with HNO_3 (1 mL per 1000 mL of sample) and refrozen until ready for extraction.

Since the sea water samples could not be adequately filtered on board at the time of collection, acidified ($\text{pH} < 5$) unfiltered samples were analyzed in the laboratory. This would allow recovery of any metals that would be lost to the polyethylene containers during shipment to the on-shore laboratory prior to acidifying.

A pH meter was used to adjust the pH of each solution to approximately 5.5 with dilute HNO_3 or NH_4OH . Next, ammonium acetate (NH_4Ac) buffer solution was added and the pH rechecked. Each solution was quantitatively transferred to a polyethylene separatory funnel and 2 mL of 2 percent APDC/DDC solution added. The solution was mixed well for 15 minutes then extracted twice with 10 mL of CHCl_3 (total of 20 mL). The organic and aqueous phases were allowed to separate and the organic extract was quantitatively transferred to a 50-mL extraction vessel. Both organic extracts (20 mL) were combined in the same extraction vessel. Next, 5 mL of 4N HNO_3 was added to the extraction vessel and the sample shaken for 15 minutes. Phases were allowed to separate, and the aqueous phase was removed to a polyethylene vial for metal analysis by flameless AAS.

4. Suspended Particulate Matter

a. Leach Procedure Using Weak Acid to Remove the Carbonate and Absorbed Elements

The Nucleopore filters (0.4 μm , 47 mm polycarbonate membranes) were stored in a desiccator for at least twenty-four hours prior to use to maintain a constant weight. The Nucleopore Swin-Lok membrane filter holders were cleaned in 8N nitric acid for four hours, rinsed with distilled water, and dried. Each filter was then preweighed in a clean bench using Teflon-coated

forceps and loaded into the filter holder. The maximum volume (2 to 3 liters) of sea water was filtered through the Nucleopore filter to improve the detection limit of those metals that normally have low concentrations in suspended particulate samples (e.g., Cd and Hg).

After filtering the maximum amount (2 to 3 liters) of sea water, each Nucleopore filter was removed from its filter holder, in a clean bench, using Teflon-coated forceps. The filter was placed in a dessicator (over silica gel) for 48 hours to dry. Once it had dried to a constant weight, the filter was weighed on the microgram balance (four decimal places) so the mass of the suspended particulate matter could be determined.

In a clean bench, the dry Nucleopore filter was placed in a 125-mL polyethylene Erlenmeyer flask and 50 mL of 25 percent (v/v) acetic acid was added. The flask was sealed to prevent contamination and then placed on a shaker for two hours at a low speed to continue leaching. Using Teflon-coated forceps, the filter pad was removed from the Erlenmeyer flask and positioned over a 100-mL Teflon beaker. The leach acid was then poured over the Nucleopore filter and collected in the Teflon beaker. The Erlenmeyer flask was rinsed three times with distilled water and poured over the filter. The filter was then rinsed twice with distilled water and the rinse added to the Teflon beaker. The filter pad was then stored in a 2" x 6" "Zip-Lock" polyethylene bag for later digestion by the rigorous method (only 10 percent of samples underwent rigorous digestion). The Teflon beaker was placed on a hot plate with low heat (approximately 100°C) and the sample concentrated to less than 10 mL. The sample was cooled and quantitatively transferred to a 10-mL volumetric flask. Distilled water was used to make the flask to the mark after 0.050 mL (50 μ L) of Suprapur HNO_3 was added to maintain the elements in solution.

This solution was then used to determine the different analyte metals using flame, flameless, or cold vapor (Hg) AAS. The concentration of the different elements determined the method of AAS analysis. A 1-mL aliquot of sample was removed for mercury determination.

b. Rigorous (Total) Digestion for the Refractory Elements

After the above leaching procedure, the refractory matter remaining on the Nucleopore filter was removed by placing the filter pad (using Teflon-coated forceps) into an all-Teflon bomb, adding 750 μL of concentrated Suprapur HCl and sealing. After digestion of the sample for two hours in a steam bath (90-100°C), the sample was cooled and the bomb opened in a clean bench and 250 μL of concentrated Suprapur HNO_3 was added. The bomb was resealed and returned to the steam bath for 30 minutes. The bomb was again removed from the water bath, cooled, opened in the clean bench, and 50 μL of concentrated HF was added. The bomb was resealed and returned to the steam bath for one hour. After allowing the bomb to cool, the digestate was quantitatively transferred to a 10-mL volumetric flask. The bomb (cap and cylinder) was rinsed three times with distilled water. The rinsings were added to the volumetric flask and distilled water was used to bring the volume to 10 milliliters.

The concentration of analyte metals in this digestate were in the range of flameless AAS except for Fe, Mn, and Zn which were analyzed by flame AAS. Hg was not determined on this aliquot.

5. Dominant Fauna

Upon arrival at the on-shore laboratory for trace metal analysis, the samples were thawed and prepared on a clean bench using Teflon-coated and stainless steel surgical instruments.

During the dissection, separate instruments were used for separate species and individuals in order to prevent cross-contamination. Between use, all dissecting instruments were cleaned according to normal laboratory procedures, washed with 0.1N nitric acid and rinsed with distilled water.

Each specimen was worked up individually with filets from left and right sides placed in an acid-washed, preweighed, 250-mL polyethylene beaker. The beakers were weighed to determine the wet weight of the muscle tissue. The sample was then frozen, freeze dried, and reweighed to determine the water loss. Next, the freeze-dried sample was ground in a Virtis "45" Homogenizer (The Virtis Company, Inc., Gardiner, New York) using stainless steel blades. This ensured complete mixing of the sample.

The finely ground sample (0.5 grams) was then weighed into a tared Pyrex ashing boat. The boat was placed into the low temperature asher (LTA-505, LFE Corporation, Waltham, Massachusetts) and the sample was ashed for 16 hours at 450 watts of forward power using an oxygen plasma. The ashing boats were removed from the asher and 1 mL of 70 percent HNO_3 (Suprapur) was added to solubilize the ash and retain it in the ashing boat during the transfer to a clean bench. The ash was quantitatively transferred into a Teflon bomb with distilled water and 3 mL of 70 percent HNO_3 (Suprapur) was added. The Teflon bomb was then sealed and placed in a steam bath (90-100°C) for two hours. The bomb was allowed to cool and the digestate was quantitatively rinsed into a 15-mL polyethylene centrifuge tube using three rinsings (both cap and cylinder) of distilled water. The sample was then centrifuged for 10 minutes at 3000 RPM. The supernatant was decanted into a 25-mL volumetric flask without disturbing the precipitate. The precipitate was then rinsed with 2 mL of distilled water and recentrifuged for 10 minutes. This rinse was then decanted into the volumetric flask and brought to volume with distilled water.

The concentrations of Cu, Fe, and Zn were great enough that aspiration into an air/acetylene flame (AAS) was used to quantitate them. Barium, Cd, Cr, Co, Pb, Mn, and Ni were quantitated using flameless AAS. Strontium was analyzed using a nitrous oxide/acetylene flame.

Because of the volatility of Hg, a special procedure was used to determine Hg in the fish tissue. A one-gram aliquot of the finely ground, freeze-dried sample was weighed into a reaction vessel. Five mL of $\text{HClO}_4\text{:HNO}_3$ (5:1) and 1 mL of KMnO_4 (5 percent solution) were added to the vessel. The vessel was shaken for five minutes, then placed in a water bath (75°C) for 30 minutes. After removing the samples from the water bath, the samples were cooled to room temperature. Next, 5 mL of distilled (Hg-free) water was added followed by 1 mL of hydroxylamine hydrochloride (50 percent). The sample was then shaken. Stannous chloride (5 percent) was added to the sample and the reaction vessel connected to the cold vapor analytical train. The Hg was purged (N_2) out of the sample and into a chamber where the light absorption occurred relative to the concentration of Hg present. Hg was quantitated by the method-of-additions using spiked samples of the material analyzed.

6. Macrocrustacea and Demersal Fish

Before dissecting, the longspine porgy and broken neck shrimp samples were weighed and measured. Only muscle tissue was used for the samples. The tissue was removed with Teflon-coated forceps and stainless steel surgical scissors after the specimen had been thawed. The excised tissue was placed in a tared freeze-drying flask and weighed. The sample was then freeze-dried and reweighed to determine weight loss. The freeze-dried tissue was thoroughly ground in a Virtis homogenizer and stored in a polyethylene bottle. A 0.5-gram aliquot of the finely ground

homogenized sample was weighed into a Pyrex ashing boat. From this point, the sample was ashed, digested, and analyzed according to the procedure given for dominant fauna analyses.

Hg was determined on a separate tissue aliquot by the cold vapor AAS method used for dominant fauna analyses. All other metals except Cu, Fe, and Zn required flameless AAS because of low concentrations.

C. Analytical Parameters and Quality Assurance

1. Sediments

A standard reference material was prepared by the 5N HNO_3 "partial" digestion procedure and analyzed for the 12 analyte metals; National Bureau of Standards, Standard Reference Material 1645, River Sediment, was prepared and analyzed for the 12 metals even though Ba and Sr were not reported for the NBS SRM River Sediment.

Table 1 summarizes the results of the analyses of NBS SRM River Sediment using the partial digestion procedure.

The NBS SRM, River Sediment, was used to calibrate a homogenous sediment sample that was prepared and routinely analyzed with the sediment samples as a quality control.

2. Suspended Particulate Matter (SPM), Sea Water and Produced Brine

Standard reference samples are not available for these sample matrices. Spiked membrane filters processed by the procedure described for SPM were used to evaluate the procedure for SPM and as quality control samples.

Artificial sea water (Riley and Skirrow, 1975) was spiked with known quantities of analyte metals and extracted using the procedure described for sea water and produced brine samples. These spiked samples were used to evaluate the extraction procedure and were periodically run as quality control samples for the sea water and produced brine analyses.

TABLE 1
TRACE METAL CONCENTRATIONS AND PERCENT RECOVERY IN NBS SRM 1645 RIVER
SEDIMENT BY PARTIAL DIGESTION PROCEDURE ($\mu\text{g/g}$ Dry wt.)

		<u>Ba</u>	<u>Cd</u>	<u>Cr*</u>	<u>Co</u>	<u>Cu</u>	<u>Fe*</u>	<u>Pb</u>	<u>Mn</u>	<u>Hg</u>	<u>Ni</u>	<u>Sr</u>	<u>Zn</u>
Reported Concentration	\bar{x}	NR	10.2	2.96	(8)**	109	11.3	714	785	1.1	45.8	NR	1720
	sd	NR	1.5	0.28	NR	19	1.2	28	97	0.5	2.9	NR	169
Determined Concentration n = 7	\bar{x}	20.2	7.23	2.26	11.1	84.2	3.94	710	398	0.69	23.6	586	1519
	sd	6.7	0.44	0.06	1.1	2.8	0.16	30	8	0.05	1.0	31	24
% Recovery		-	71	76	(139)	77	35	99	51	63	52	-	88

* weight %

** value not certified

NR = not reported

3. Biota

National Bureau of Standards, Standard Research Material 1577, Bovine Liver, was prepared and analyzed using the methodology described for dominate fauna analyses to evaluate the procedure.

A large homogenous sample of fish muscle tissue was prepared and periodically analyzed (spiked and unspiked) as a means to quantitate the biota data ("method of additions") and to act as a routine quality control.

Table 2 summarizes the results of the analyses of NBS SRM 1577, Bovine Liver.

TABLE 2

TRACE METAL CONCENTRATIONS AND PERCENT RECOVERY IN NBS SRM 1577
BOVINE LIVER ($\mu\text{g/g}$ Dry wt.)

		<u>Ba</u>	<u>Cd</u>	<u>Cr</u>	<u>Co</u>	<u>Cu</u>	<u>Fe</u>	<u>Pb</u>	<u>Mn</u>	<u>Hg</u>	<u>Ni</u>	<u>Sr</u>	<u>Zn</u>
Reported Concentration	\bar{x} sd	NR NR	0.27 0.04	NR NR	(0.18)*	193 10	270 20	0.34 0.08	10.3 1.0	0.016 0.002	NR NR	(0.14)*	130 10
Determined Concentration n = 7	\bar{x} st	4.78 0.16	0.43 0.05	1.19 0.12	0.18 0.00	188 3	252 26	0.31 0.08	9.48 0.00	0.015 0.001	0.19 0.00	0.15 0.00	138 5
% Recovery		-	119	-	(100)	97	93	91	92	94	-	(107)	106

* value not certified

NR = not reported

III. RESULTS AND DISCUSSION

A. Surficial Sediments

Sediments are the final repository of all trace metals in the marine environment. Sediment trace metal burdens can provide important information on what influence man's activities have had on the marine environment and ecology.

Anderson and Schwarzer (1979) have shown that surficial sediment concentrations of Ba, Pb, Sr and Zn are significantly above background levels within 180 meters of the platform structures. They determined these increases by comparing the surficial sediment concentrations with downcore sediments concentrations at a core depth that would reflect the predevelopment era of the Buccaneer Oilfield and by comparing with surficial sediment concentrations from an undeveloped area (South Texas Outer Continental Shelf Study)(Berryhill, 1975).

This year's sediment investigations have been concentrated on the near-field environment of the Buccaneer oilfield. Since the platforms have produced brine discharges and more activities that could add metal pollution to the marine environment, a well jacket (288-5) (see Figure 1, page 2.4.2-47) was selected as a control station to which comparisons could be made. The well jacket is not an ideal control, but it can simulate the platform structures and it does not have the discharges the platforms have. Also, it is relatively close to the platforms and would be subjected to the same natural variances (winds, currents, storm fronts, etc.) that would effect the sediment trace metal burdens at the platforms.

Surficial sediments from the area of platforms 288-A and 296-B show distinct concentration gradients for several trace metals (Ba, Cd, Cr, Cu, Mn, Pb, Sr, Zn). There appears to be

a strong seasonal effect on both the concentration gradients and the overall trace metal concentration at both platforms.

Figures 2 through 13 and 14 through 25 are graphical representations of the concentration gradients and seasonal variability at platforms 288-A and 296-B, respectively. In the fall season (Cruise II) and spring season (Cruise IV), a reduced sampling effort was conducted at the 25-meter stations only. Therefore, no statement can be made about concentration gradients during these two seasons. However, the overall seasonal variability of trace metals in surficial sediments can be estimated based on the available data.

At platform 288-A, there appears to be a strong seasonal variation in Ba, Cd, Cu, Pb, Ni, and Zn (Figures 2, 3, 6, 11, 10, 13). There is a suggestion of seasonal variability in Hg at platform 288-A (Figure 8). The remaining metals (Co, Fe, Mn) appear to be relatively consistent through all seasons with occasional high values.

Summer (Cruise I) season sediments have the highest metal concentrations and the strongest suggestion of concentration gradients, while the winter samples (Cruise III) have the lowest concentrations of Ba, Co, Cu, and Hg.

At platform 296-B, there are seasonal variations in Ba, Cr, Pb, Sr, and Zn (Figures 14, 17, 23, 24, and 25). The remaining metal (Cd, Co, Cu, Fe, Mn, Hg, Ni) concentrations appear not to vary seasonally.

Seasonal variations in the sediment trace metal burdens are probably due to the very dynamic bottom caused by the strong currents and wave action around the platform structures (Anderson and Schwarzer, 1979; Brooks, Estes and Huang, in preparation). These currents and wave actions cause a significant amount of continuous scouring and resuspension of bottom sediments which causes changes in sediment texture and characteristics that can affect the trace metal composition.

Tables 3, 4, and 5 are the average trace metal concentrations, by season, for platforms 288-A, 296-B, and flare stack 296-B/well jacket 288-5, respectively.

At platforms 288-A and 296-B (Tables 3 and 4) there appears to be less overall variability in metal concentrations during the winter sampling (Cruise III). The highest variability is in Cd, Hg, and Zn. There are high seasonal variabilities for metals which are due to one or two unusually high samples for that season. Examples of these are Cu and Pb in the summer at 288-A (Table 3), Sr in the fall and Cr during the spring at 296-B (Table 4).

Comparison of the overall seasonal mean concentrations with the 288-5 well jacket "control" (Table 5) does not show any significant trends; however, there are consistently higher Cu and Zn concentrations at the well jacket than at the platforms or flare stack.

A means of assessing the trace metal concentration gradients at the platforms is to construct scatter plots of the metal concentrations versus the Fe concentration (Trefrey and Presley, 1977). Since Fe, as compared to other transition elements, is in relatively high concentration in the sediments, only catastrophic inputs would seriously effect its concentration. Therefore, in unaltered sediments, correlation between the Fe values and other transition metal values should be very good. By plotting these metal values versus Fe values and determining the best-fit linear equations and correlation coefficients (R^2), any abnormal metal inputs to the sediments can be identified.

Figures 26 through 47 are scatter plots of the sediment metal concentrations versus the Fe concentration by season. These plots include all sediment samples analyzed during a season. Best-fit linear regression equations with their R^2 value are given for each season.

Table 3
SEASONAL COMPARISON OF AVERAGE TRACE METAL CONCENTRATIONS ($\mu\text{g/g}$ DRY WT) IN SURFICIAL SEDIMENTS
FROM PLATFORM 288-A

Cruise	Axis	Ba	Cd	Co	Cr	Cu	Fe**	Hg	Mn	Ni	Pb	Sr	Zn
I (Summer)	N	136	1.42	4.48	10.6	21.3	0.82	0.330	336	8.78	84.8	630	1680
	E	81	0.50	4.55	10.5	48.2	0.54	0.098	214	13.6	45.8	418	301
	S	83	0.55	5.45	7.45	8.6	0.59	0.482	297	7.44	82.5	212	341
	W	90	0.45	4.33	9.06	12.2	0.66	0.027	263	7.76	69.6	373	1801
	Structure	179	1.17	4.39	17.1	20.7	0.49	0.101	566	8.20	1588	754	2356
	Mean	109	0.80	4.70	10.5	22.3	0.63	0.215	319	9.22	287	464	1220
	SD	58	0.83	0.85	4.9	23.0	0.23	0.274	195	5.41	808	322	1635
	CV %	52.3%	104%	18.1%	46.7%	103%	36.5%	127%	61.1%	58.7%	282%	69.4%	134%
II (Fall)	N	22	0.10	3.94	5.50	9.78	0.69	0.135	221	7.24	36.4	163	486
	E	15	0.15	4.27	6.78	8.83	0.65	0.144	133	9.29	52.7	72.7	593
	S	43*	0.79*	3.15*	15.5*	10.3*	1.49*	0.164*	295*	7.10*	176*	499*	3521*
	W	28	0.34	4.39	6.93	12.5	0.80	0.163	175	9.83	53.5	130	291
	Structure	31*	0.38*	2.47*	11.5*	34.9*	0.61*	0.123*	180*	6.28*	120*	936*	1420*
	Mean	28	0.35	3.64	9.24	15.3	0.85	0.146	201	7.95	87.7	360	1262
	SD	10	0.27	0.82	4.17	11.1	0.37	0.018	61	1.53	58.9	362	1334
	CV %	37.7%	77.4%	22.4%	45.2%	72.5%	43.1%	12.2%	30%	19.2%	67.1%	101%	106%
III (Winter)	N	7.8	0.13	5.07	6.08	8.20	0.46	0.390	163	4.46	46.0	307	444
	E	12	0.18	3.07	8.23	6.47	0.61	0.062	204	5.28	189	509	1129
	S	12	0.09	2.73	8.13	7.38	0.51	0.114	196	5.07	33.6	201	311
	W	10	0.07	3.80	5.92	5.55	0.57	0.035	223	4.66	51.5	169	312
	Structure	20	0.40	5.34	11.1	9.06	0.65	1.223	205	4.33	109	168	697
	Mean	12	0.17	4.00	7.89	7.33	0.56	0.365	198	4.76	87.7	271	579
	SD	4.4	0.13	1.17	2.10	1.38	0.08	0.500	22.0	0.40	63.2	145	346
	CV %	35.9%	76.5%	29.2%	26.6%	18.9%	13.5%	137%	11.1%	8.48%	72.1%	53.5%	59.7%
IV (Spring)	N	11	0.29	3.52	23.6	10.2	0.52	0.210	215	4.07	129	226	638
	E	22	0.30	2.95	11.4	9.68	0.63	0.152	281	5.50	118	366	1439
	S	35	0.22	4.66	16.1	23.4	0.91	0.051	262	7.95	137	221	972
	W	19	0.09	4.54	6.51	4.86	0.67	0.024	234	4.20	67.1	146	166
	Structure	29	0.16	4.32	6.85	20.9	0.76	0.201	243	6.40	62.1	181	510
	Mean	23	0.21	4.00	12.9	13.8	0.70	0.128	247	4.62	102	228	745
	SD	9.1	0.09	0.74	7.15	7.94	0.15	0.086	25.5	1.62	35.4	83.7	484
	CV %	39.4%	41.8%	18.4%	55.5%	57.5%	21.1%	67.2%	10.3%	28.8%	34.5%	36.7%	64.9%

* shell hash

** concentration in %

Table 4
SEASONAL COMPARISON OF AVERAGE TRACE METAL CONCENTRATIONS ($\mu\text{g/g}$ DRY WT) IN SURFICIAL SEDIMENTS
FROM PLATFORM 296-B

Cruise	Axis	Ba	Cd	Co	Cr	Cu	Fe**	Hg	Mn	Ni	Pb	Sr	Zn
I (Summer)	N	44	1.08	4.59	6.87	4.9	0.44	0.050	169	5.90	21.7	212	259
	E	100	0.64	4.10	7.46	5.0	0.41	0.032	170	5.83	82.1	335	574
	S	77	0.35	4.11	8.60	13.9	0.54	0.123	167	7.23	29.0	251	300
	W	81	3.45	4.20	9.83	8.7	0.56	0.103	172	6.44	88.3	172	429
	Structure	187	5.66	4.39	16.8	20.5	0.83	0.049	190	9.43	55.6	729	1746
	Mean	88	1.67	4.22	8.90	9.1	0.51	0.073	171	6.58	60.0	289	519
	SD	55	2.78	0.44	2.98	7.5	0.15	0.084	15	1.72	52.7	219	552
	CV %	62.5%	166%	10.4%	33.5%	82.4%	29.4%	115%	8.8%	26.1%	87.8%	75.8%	106%
II (Fall)	N	43	0.31	4.50	7.91	11.1	0.74	0.106	169	8.06	60.2	186	1478
	E	111*	0.74*	2.14*	6.48*	6.95*	0.43*	0.015*	107*	4.51*	386*	2558*	2120*
	S	37	0.13	3.37	7.68	6.32	0.71	0.153	207	6.96	44.3	625	428
	W	15	0.08	3.71	3.99	2.64	0.58	0.032	169	7.24	21.3	270	196
	Structure	15	0.09	4.05	4.44	3.69	0.60	0.054	177	5.33	16.7	55.1	195
	Mean	42	0.27	3.55	6.10	6.14	0.61	0.072	166	6.42	106	739	883
	SD	41	0.28	0.89	1.81	3.30	0.12	0.057	36	1.46	158	1039	871
	CV %	98.3%	103%	25.2%	29.7%	53.7%	20.1%	78.8%	22%	22.7%	149%	141%	98.6%
III (Winter)	N	23	0.07	4.35	6.85	5.44	0.55	0.137	180	4.76	66.9	145	211
	E	25	0.11	4.01	9.76	4.17	0.57	0.096	180	4.29	90.1	260	498
	S	24	0.19	4.20	6.18	3.47	0.53	0.168	171	4.66	33.6	134	967
	W	25	0.07	3.52	6.49	6.09	0.55	0.092	183	4.85	45.0	129	123
	Structure	41	0.22	4.54	11.8	8.03	0.61	0.036	195	4.20	60.9	267	859
	Mean	27	0.13	4.12	8.22	5.44	0.56	0.106	182	4.55	59.3	187	532
	SD	7.4	0.07	0.39	2.46	1.78	0.03	0.050	8.64	0.29	21.6	70.1	377
	CV %	27.2%	52.6%	9.45%	30.0%	32.7%	5.35%	47.2%	4.75%	6.37%	36.5%	37.5%	70.9%
IV (Spring)	N	14	0.04	2.06	2.58	1.70	0.33	0.012	104	3.04	< 2.16	48.2	170
	E	19	0.12	4.56	5.01	14.8	0.53	0.222	187	4.72	22.8	101	276
	S	14	0.06	5.51	5.44	6.92	0.61	0.188	238	4.85	57.8	140	151
	W	30	0.04	4.80	5.19	3.59	0.49	0.056	179	3.43	40.0	81.0	96.7
	Structure	75	0.53	4.20	35.8	21.7	1.05	0.217	231	7.44	403	404	3692
	Mean	31	0.16	4.23	10.8	9.74	0.60	0.139	188	4.70	105	155	877
	SD	26	0.21	1.30	14.0	8.35	0.27	0.098	53.6	1.72	168	143	1575
	CV %	84.3%	133%	30.8%	130%	85.7%	44.9%	70.5%	28.5%	36.7%	160%	92.5%	180%

* shell hash

** concentration in %

Table 5
SEASONAL COMPARISON OF TRACE METAL CONCENTRATIONS ($\mu\text{g/g}$ DRY WT) IN SURFICIAL SEDIMENTS
FROM FLARE STACK AND WELL JACKET

<u>Cruise</u>	<u>Ba</u>	<u>Cd</u>	<u>Co</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe**</u>	<u>Hg</u>	<u>Mn</u>	<u>Ni</u>	<u>Pb</u>	<u>Sr</u>	<u>Zn</u>
<u>Flare Stack</u>												
I - Summer	24.3	0.05	3.90	3.94	1.77	0.27	0.008	210	3.18	2.88	67.8	22.2
II - Fall	12	0.02	3.71	3.47	1.70	0.46	0.014	178	4.23	3.35	52.6	22.2
III - Winter	<4.2	0.004	4.32	4.30	1.95	0.45	<0.009	182	3.94	12.5	154	17.4
IV - Spring	8.1	0.03	3.63	3.17	1.96	0.44	<0.009	206	3.30	4.73	138	19.3
<u>Well Jacket</u>												
I - Summer	240	0.70	4.14	13.8	14.6	0.40	0.049	891	5.50	96.6	1017	1094
II - Fall	43*	0.24*	360*	6.63*	7.57*	1.34*	0.752*	400*	7.37*	38.9*	1404*	2781*
III - Winter	28	0.13	6.25	6.54	41.2	0.94	0.039	401	6.79	60.9	300	1464
IV - Spring	35	0.08	2.50	8.78	11.8	0.77	0.042	314	6.27	44.4	236	751

* shell hash

** concentration in %

2.4.2-20

There are two samples with unusually high Fe concentrations in the fall season which tend to distort the regression lines for Ba, Co, Cu, Ni, and Pb (Figures 26, 30, 34, 40, and 42, respectively).

Examination of the scatter plots shows some interesting trends. The summer season showed more scatter for Ba, Cd, Cr, Cu, Mn, Pb, Sr, and Zn. There is also a moderate amount of scatter in Cd, Cr, Sr, Mn, and Zn during the fall season. Mercury has relatively little scatter during the summer and fall but significantly more during the winter and spring.

Scatter plots of Ba, Cd, Cr, Cu, Mn, Pb, Sr, and Zn for the winter and spring show less scatter as compared to the summer and fall.

Nickel and Co show little scatter through all four seasons.

The regression equations and correlation coefficients (R^2) for the fall, winter, and spring seasons can be improved by elimination of one or more unusually high values. For example, in Figure 45 for Sr, the negative slope of the regression line is reversed and the R^2 value increases to 0.1687 by elimination of the two values above 1000 ppm Sr.

It is important to note that the majority of data points with an unusually high Y-axis scatter are at those stations near (0 and 25 meters) the platform structures. This would suggest that the source of these increased metal concentrations could be related to the platform structures or the petroleum production activities on them.

Comparison of these scatter plots with others from areas of the Gulf that are not considered to be contaminated (Trefry and Presley, 1976; Shokes, 1978; Tillery, in preparation) illustrate the abnormality of the situation near these platform structures. Comparison of these linear regression equations with those from noncontaminated areas can give an estimate of the natural concentrations

of trace metals in sediments and indicate if there are significant increases in sediment trace metal concentrations near the platform structures.

Table 6 is a comparison of the normal trace metal concentration in sediments, developed from linear regression equations (metal concentration versus Fe concentrations), from two studies, representative of noncontaminated areas of the Gulf, with concentrations derived from the summer cruise samples (Cruise I). A third comparison is made to the normal concentrations developed from plots of trace metal concentrations from diver-collected core samples taken during the second year (1977-1978) of the BOF study. These sediment core samples were collected at platform 288-A and satellite structure. Only the bottom core samples were used since Anderson and Schwarzer (1979) indicated these were representative of the predevelopment period of the BOF.

There is an apparent accumulation of Cr, Hg, Pb, Sr and Zn in sediment when compared to the ambient levels developed from the core samples (second year BOF). Compared to the Louisiana Platform Study values, Pb would not be accumulating in the BOF sediments. However, the Louisiana Platform Study samples were collected in the offshore oilfields and may actually show some accumulation from this source.

Sediment characteristics can cause variations in the trace metal content of sediments. Trace metal concentrations and sediment grain size have an inverse relationship which is thought to be caused by the increased surface area (i.e., adsorption sites) available for metal binding. Unaltered sediments should have a positive regression slope and good correlation in a scatter plot of grain size (ϕ) versus metal concentration.

Figures 48 and 49 are seasonal scatter plots of sediment Fe concentration versus grain size (ϕ) showing the best fit linear

Table 6

COMPARISON OF AMBIENT SEDIMENT TRACE METAL BURDENS ($\mu\text{g/g}$) DEVELOPED
FROM REGRESSION EQUATIONS (METAL CONCENTRATION VS FE CONCENTRATIONS)
WITH SEDIMENT BURDEN IN SUMMER CRUISE (I) SAMPLES.

Metal	1978-79 BOF Summer Cruise	Trefry & Presley 1976	BLM-1978-79 Louisiana Platform Study	1977-78 BOF Core Samples ⁽¹⁾
	I		Tillery in preparation	Anderson & Schwarzer 1979
Ba	51	ND	39.5	112
Cd	0.124	0.056	0.131	5.46 ⁽²⁾
Co	3.74	NR	ND	-2.35
Cr	2.5	NR	1.68	0.53
Cu	0.5	1.41	2.79	0.47
Hg	-0.174	ND	ND	0.067
Mn	123	NR	ND	177
Ni	1.19	1.72	4.40	-2.82
Pb	7.37	2.03	8.63	0.83
Sr	187	ND	ND	25
Zn	-826	-2.40	22.8	20.8

(1) only bottom core samples used

(2) only 3 data points used to develop this value; \leq values not used

ND = metal not determined

NR = data not reported

equation and correlation coefficient. There is very poor correlation in any season. Other metals (except Co) had poor correlation with sediment grain size through all four seasons. However, there was good correlation of Co during the summer ($R^2 = 0.54$) and fall ($R^2 = 0.57$) seasons.

This lack of correlation with sediment grain size (Brooks et al., in preparation) is further evidence that the trace metal gradients of Ba, Cd, Cr, Cu, Mn, Pb, Sr, and Zn observed at the platform structures are related to the structures or the petroleum production activities on them. These metals include those (Ba, Sr, Cd, Co, Pb) that Wheeler (1979) found by cluster analysis to be associated with anthropogenic inputs.

B. Suspended Particulate Matter, Sea Water and Produced Brine

Platform 296-B was actively discharging production waters (brine) to the marine water column during this year's investigation. Platform 288-A was not discharging production brine during this year's sampling but has been actively discharging in the recent past. Previous investigations of these production brines (Anderson and Schwarzer, 1979) has shown that the average concentrations of Sr and Ba from platform 296-B were 33.5 ppm and 3.5 ppm, respectively. By examining these production brines, sea water and suspended particulate matter (SPM), the transport and fate of the trace metals introduced to the marine environment from this source may be determined.

Table 7 is the seasonal average trace metal concentrations in SPM from Platforms 288-A, 296-B, well jacket 288-5, and flare stack 296-B. The trace metal burdens in SPM samples are known to be highly variable. However, by comparing to a control sample (well jacket), an estimation of the trace metal input from the produced brine discharge may be made. Also, by normalizing the

Table 7
AVERAGE SEASONAL TRACE METAL CONCENTRATIONS ($\mu\text{g/g}$) IN SUSPENDED PARTICULATE MATTER

Cruise	Location	Ba	Cd	Cr	Co	Cu	Fe	Pb	Mn	Hg	Ni	Sr	Zn
I Summer	288-A	357	41.9	435	29.1	324	4301	294	670	38.1	537	140	1012
	296-B	319	34.2	185	31.2	135	3446	149	354	40.8	301	159	1001
	Well Jacket *	31	10.8	81	7.4	39	1670	14	444	9.7	50	104	238
	Flare Stack **	172	24.2	14	16.6	79	1792	31	597	2.4	18	91	534
	x	317	36.1	335	28.6	210	3668	201	506	36.6	380	145	952
	sd.	309	17.0	492	12.8	251	4733	388	304	18.0	382	58	464
	RSD(%)	97	47	147	45	120	129	193	60	49	101	40	49
n=23													
II Fall	288-1	86	9.1	42	7.8	57	1235	42	843	6.2	287	131	251
	296-B	83	70.0	67	9.5	73	1053	17	361	11.1	135	77	262
	Well Jacket *	58	9.7	77	6.7	29	130	12	3	8.8	61	47	215
	Flare Stack **	55	12.8	42	9.4	42	458	6	257	12.3	97	153	302
	x	77	35.1	55	8.7	59	938	23	475	9.5	173	105	261
	sd.	34	59.8	44	3.6	37	488	22	410	6.8	293	55	128
	RSD(%)	44	170	80	41	63	52	96	86	72	169	52	49
n=12													
III Winter	288-A	20	16.0	22	11.2	91	885	35	1170	14.7	128	160	272
	296-B	56	33.6	47	9.8	69	1375	15	1064	13.1	85	156	321
	Well Jacket *	37	17.3	12	11.9	26	115	22	3751	15.5	101	182	381
	Flare Stack **	74	11.4	8	7.9	17	838	15	380	10.3	66	108	252
	x	43	25.4	35	10.3	73	1115	23	1193	13.7	101	156	303
	sd.	67	51.3	42	4.0	93	782	17	849	3.9	72	25	187
	RSD(%)	156	202	120	39	127	70	74	71	28	71	16	62
n=22													
IV Spring	288-A	74	5.4	14	7.8	230	3417	12	1786	6.6	42	68	141
	296-B	67	10.4	11	9.8	344	2963	27	1514	11.1	83	88	269
	Well Jacket *	136	11.6	8	8.4	134	4386	19	1365	10.5	68	63	39
	Flare Stack **	58	0.2	9	19.7	15	3693	16	1222	0.4	54	96	284
	x	75	7.6	12	9.7	252	3415	20	1590	8.3	62	79	198
	sd.	30	7.4	11	5.3	228	558	10	528	7.2	40	20	143
	RSD(%)	40	97	92	55	90	16	50	33	87	65	25	72
n=12													

* Well Jacket 288-5

** Flare Stack 296-B

SPM trace metal concentrations to their hydrous Fe concentration and comparing to sediment data similarly normalized, the amount of SPM from resuspension of fine grain sediments can be estimated.

Examination of Table 7 shows that well jacket samples during the summer have lower trace metal concentrations except for Mn, which is similar to the other structures. The fall samples have similar concentration of metals except for Fe, Pb, Mn, Ni and Sr which are lower at the well jacket station. The winter and spring sample concentrations are similar except for a high Mn concentration at the well jacket during the winter. Since there are similar trace metal concentrations at both platforms and the flare stack, the inputs from the produced brine discharge cannot be determined.

Table 8 is the mean trace metal concentrations from Table 4 (sediments) and Table 7 (SPM) normalized with the hydrous Fe concentrations. This allows a comparison between the normalized sediment and SPM trace metal concentrations such that the contribution from resuspension of bottom sediment can be determined. In the summer, fall and winter, only Pb appears to be associated with resuspended sediments. In the spring, Sr in the SPM may come from resuspended sediments.

Table 8 also shows there are similar concentrations of all metals at platforms 288-A and 296-B. The higher concentrations of metals in the SPM may be from (1) the smaller size particles, (2) the organic materials present in the SPM, or (3) from the platform structures.

The average seasonal trace metal concentrations in sea water and produced brine are given in Table 9. There does not appear to be any seasonal trends in the metal concentrations of the produced brine samples. However, there does appear to be a higher concentration of Cd, Pb and Zn in the samples taken in the summer.

Table 8
SEASONAL COMPARISON OF NORMALIZED (TO FE) MEAN CONCENTRATIONS IN SPM WITH NORMALIZED (TO FE)
MEAN TRACE METAL CONCENTRATIONS IN SURFICIAL SEDIMENT

<u>Cruise</u>		<u>Ba</u>	<u>Cd</u>	<u>Cr</u>	<u>Co</u>	<u>Cu</u>	<u>Pb</u>	<u>Mn</u>	<u>Hg</u>	<u>Ni</u>	<u>Sr</u>	<u>Zn</u>
SPM	Summer I	864.2	98.15	913.3	77.97	572.5	548.0	1379	99.78	1036	395.3	2595
	Fall II	820.9	374.2	586.4	92.75	629.0	245.2	5064	101.28	1844	1119	2783
	Winter III	385.7	227.8	313.9	92.38	654.7	206.3	10700	122.9	905.8	1399	2717
	Spring IV	219.6	22.54	35.14	28.40	737.9	58.57	4656	24.30	181.6	231.3	579.8
Sediments	Summer I A*	173.1	1.270	16.67	7.460	35.40	455.6	506.3	0.3413	14.63	736.5	1937
	Summer I B*	172.5	3.275	17.45	8.275	17.84	117.6	335.3	0.143	12.90	566.7	1018
	Fall II A*	32.94	0.4118	10.87	4.282	18.00	103.2	236.5	0.172	9.353	423.5	1485
	Fall II B*	68.85	0.4426	10.00	5.820	10.07	173.8	272.1	0.118	10.525	1211	1448
	Winter III A*	21.43	0.3036	14.09	7.143	13.09	156.6	353.6	0.6518	8.500	483.9	1034
	Winter III B*	48.21	0.2321	14.68	7.357	9.714	105.9	325.0	0.1893	8.125	333.9	950
	Spring IV A*	32.86	0.3000	18.43	5.714	19.71	145.7	352.9	0.1829	6.600	325.7	1064
	Spring IV B*	51.67	0.2667	18.00	7.050	16.23	175.0	313.3	0.2317	7.833	258.3	1462

* Platform

Table 9
SEASONAL CONCENTRATIONS ($\mu\text{g/L}$) OF TRACE METALS IN SEA WATER AND
PRODUCED BRINE SAMPLES

Cruise	Site	(m) Distance	Number of Samples Averaged	Ba	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sr*	Zn
I (Summer)	A	0	1	21	0.005	<0.07	0.03	0.52	<0.51	0.056	0.17	0.07	0.59	12.3	3.2
	B	0	1	26	<0.002	<0.07	0.03	0.18	2.20	0.072	0.02	0.10	0.27	11.1	0.8
		25	4	21	0.031	<0.07	0.02	0.77	2.55	0.058	0.07	0.12	1.22	11.2	3.3
		100	1	16	0.016	0.07	0.03	0.43	1.38	0.059	0.02	0.02	0.21	9.7	3.9
	Flare	25	1	21	0.018	<0.07	0.01	0.54	4.13	0.033	<0.01	0.02	0.49	12.6	3.0
	Well Jacket	0	1	25	0.009	<0.07	0.01	0.49	2.62	0.069	<0.01	0.04	1.21	10.9	1.8
		25	1	16	0.042	<0.07	0.26	0.43	4.82	0.071	0.23	0.18	0.78	12.9	3.5
	B-Produced Brine	0	2	1548	0.167	<0.07	1.03	0.59	339.50	0.121	0.68	0.29	2.93	58.1	47.7
II (Spring)	A	0	1	13	0.006	<0.07	0.02	0.40	<0.51	0.049	<0.01	0.05	0.38	13.2	1.2
		25	1	19	0.011	<0.07	0.02	0.54	0.96	0.062	0.02	0.09	0.55	9.9	2.8
	B	0	1	17	0.005	<0.07	0.02	0.22	<0.51	<0.027	0.04	0.32	2.85	11.1	1.6
		25	1	17	0.007	<0.07	0.01	0.36	<0.51	0.069	<0.01	0.02	0.67	10.5	4.6
	Flare	25	1	17	0.010	<0.07	0.01	0.47	<0.51	0.046	<0.01	0.05	0.64	9.0	7.9
	Well Jacket	0	1	17	<0.002	<0.07	0.09	0.55	<0.51	<0.027	0.06	0.03	0.91	13.4	1.6
	B-Produced Brine	0	1	1542	0.003	<0.07	0.73	0.14	203.00	0.086	0.65	0.41	0.42	64.1	1.6
III (Winter)	A	0	1	23	0.023	0.08	0.04	0.51	5.37	0.056	0.07	0.98	2.35	13.2	3.4
		25	1	22	0.003	<0.07	0.06	0.58	<0.51	<0.027	<0.01	0.06	0.40	11.6	2.3
		100	2	25	0.009	<0.07	0.45	0.52	1.86	<0.043	0.02	0.10	0.63	11.7	2.0
	B	0	1	24	0.010	<0.07	0.03	0.68	16.40	0.038	0.08	0.05	1.83	11.3	5.4
		50	1	22	0.017	<0.07	0.03	0.50	9.36	<0.027	0.03	0.13	1.00	12.7	6.1
		100	1	23	0.007	<0.07	0.04	2.20	1.24	0.036	0.01	0.12	5.24	12.2	4.8
	Flare	25	1	26	<0.002	0.18	0.72	0.37	1.51	0.056	0.01	0.09	0.37	12.1	1.6
	Well Jacket	0	1	19	0.003	<0.07	0.03	0.52	3.58	0.056	0.01	0.04	1.27	12.2	1.6
		25	1	23	0.004	<0.07	0.03	0.54	1.79	0.027	0.03	0.07	0.50	12.4	1.2
	B-Produced Brine	0	2	1029	0.014	<0.07	1.45	1.01	379.50	0.110	1.27	0.62	0.93	67.0	3.5
IV (Fall)	A	0	1	27	0.008	<0.07	0.02	0.38	0.69	<0.027	0.02	0.09	0.48	12.4	2.3
	B	0	1	23	0.013	<0.07	0.01	0.40	1.38	<0.027	0.38	0.03	0.72	11.7	10.3
		25	1	24	0.009	<0.07	0.02	0.31	4.27	<0.027	0.03	0.10	0.78	8.8	2.9
	Flare	25	1	26	0.019	0.08	0.35	0.41	10.50	<0.027	0.07	0.24	0.78	10.9	5.2
	Well Jacket	0	1	20	0.007	<0.07	65.10	0.56	0.55	0.072	0.04	0.03	168.0	12.5	2.7
		25	1	15	0.005	0.10	0.02	0.35	1.51	<0.027	0.08	<0.01	0.32	6.6	4.1
	B-Produced Brine	0	1	1056	0.045	<0.07	0.09	0.47	118.00	0.424	0.76	0.09	0.54	93.6	7.8

* Strontium reported in $\mu\text{g/mL}$ (ppm).

No cause for a seasonal difference in the produced brine waters is known.

Comparing the trace metal concentrations in produced brine discharge from platform 296-B with the sea water collected from around 296-B (Table 9) indicates an enrichment of Cd, Cr, Fe, Hg, Mn, Ni, Pb, Sr and Zn in the produced brine during the summer. However, only Cr, Fe and Mn continue to be enriched through the other three seasons. Barium and Sr are higher through all seasons.

These higher concentrations of Cr, Fe, Mn, Ba and Sr in produced brine can be a significant source of these metals to the sediments and SPM. Also, our Ba concentrations in produced brine from platform 296-B are similar to the average concentration reported last year (3.5 ppm)(Anderson and Schwarzer, 1979). Our Sr concentrations are about twice the average concentration reported last year (33.5 ppm)(Anderson and Schwarzer, 1979).

Trace metal concentrations in sea water are low (for unfiltered sea water) and no seasonal trends were observed. There are no apparent correlations in sea water metal concentrations and the platform or satellite structures.

C. Fish and Shrimp

Pelagic fish were collected in four consecutive seasons from the vicinity of platforms 288-A, 296-B and well jacket 288-5. Two species were sampled, Archosargus probatocephalus (sheepshead) and Chaetodipterus faber (spadefish). One species of demersal fish, Stenotomus caprinus (longspine porgy), was substituted for macrocrustacean samples during the summer cruise. Macrocrustacean samples collected in the fall, winter, and spring seasons were Trachypenaeus similis (sugar shrimp).

Only muscle tissue of fish and shrimp were analyzed for trace metals. Comparison of the seasonal mean trace metal concentrations in sheepshead, spadefish and longspine porgy with other Gulf studies are presented in Tables 10, 11, and 12, respectively.

Table 10
COMPARISON OF SEASONAL VARIATIONS IN AVERAGE TRACE METAL CONCENTRATIONS ($\mu\text{g/g}$ DRY WT)
IN ARCHOSARGUS PROBATOCEPHALUS (SHEEPSHEAD) MUSCLE TISSUE WITH OTHER GULF STUDIES

	Cruise		Ba	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sr	Zn
Buccaneer Oilfield	Summer n=8	\bar{x}^*	<0.88	0.031	<0.30	0.245	0.59	8.5	0.354	0.37	0.561	0.129	19.9	13.5
		sd.	--	0.032	--	0.055	0.17	2.8	0.155	0.07	0.257	0.034	3.5	1.1
		RSD%	--	103	--	22	29	33	44	20	46	26	18	8
	Fall n=12	\bar{x}^*	1.1	0.146	0.32	0.890	1.51	9.6	0.170	0.47	0.625	0.501	2.0	12.1
		sd.	0.51	0.103	0.05	0.566	0.62	6.4	0.120	0.10	0.193	0.644	2.3	1.5
		RSD%	46	71	16	64	41	67	70	21	31	129	115	12
	Winter n=19	\bar{x}^*	1.3	0.376	0.62	0.606	1.40	12.5	0.426	0.59	0.978	0.757	4.6	14.7
		sd.	0.66	0.964	0.46	0.483	0.68	3.8	0.217	0.16	0.529	0.899	5.3	3.4
		RSD%	51	256	75	80	49	30	51	26	54	119	115	23
	Spring n=12	\bar{x}^*	3.4	0.240	0.37	2.65	0.99	27.3	0.672	0.51	0.532	0.185	3.8	27.3
		sd	1.6	0.280	0.09	2.92	0.19	16.1	0.594	0.12	0.242	0.096	1.5	16.1
		RSD%	47	117	23	110	19	59	88	23	45	52	39	59
Louisiana Platform Study ¹	Range		<0.011- 0.057		<0.20- 2.03		0.57- 2.18	12.4- 35.7			<0.38- 2.33	<0.110- 0.210		9.2- 18.1
	\bar{x}^*	NA	0.052	ND	1.04		1.13	20.6	ND	ND	1.17	0.128	ND	13.9
	RSD%		8.8		70		46	43			54	30		18

1. Tillery, 1979

* Those samples at or below detection limit included as detection limit value.

ND = Not determined

NA = Data not available

Table 11
COMPARISON OF SEASONAL VARIATIONS IN AVERAGE TRACE METAL CONCENTRATIONS ($\mu\text{g/g}$ DRY WT) IN
CHAETODIPTERUS FABER (SPADEFISH) MUSCLE TISSUE WITH OTHER GULF STUDIES

	Cruise	Ba	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sr	Zn		
Buccaneer Oilfield	Summer n=8	\bar{x}^* sd. RSD%	<0.88 -- --	0.032 0.022 69	<0.30 -- --	0.223 0.061 27	0.53 0.08 15	8.8 3.3 38	0.222 0.076 34	0.52 0.27 52	1.04 0.75 72	0.130 0.040 31	22.4 2.5 11	17.7 2.0 11	
	Fall n=12	\bar{x}^* sd. RSD%	1.2 0.5 45	0.158 0.067 42	0.39 0.22 56	0.966 0.533 55	1.72 0.62 36	10.8 6.8 63	0.140 0.074 53	0.38 0.08 21	0.88 0.72 82	0.300 0.132 44	1.35 1.20 89	16.2 4.3 26	
	Winter n=18	\bar{x}^* sd. RSD%	1.2 0.5 45	0.132 0.048 36	0.67 0.56 83	0.764 0.825 108	3.25 4.87 150	13.3 5.5 42	0.283 0.091 32	0.49 0.12 25	1.32 0.65 49	0.531 0.383 72	3.49 1.95 56	17.8 3.0 17	
	Spring n=12	\bar{x}^* sd. RSD%	3.6 1.4 39	0.186 0.232 125	0.39 0.18 47	1.17 1.15 98	1.02 0.20 20	22.0 10.6 48	0.274 0.077 28	0.56 0.08 14	0.46 0.19 41	0.249 0.224 90	2.35 0.73 31	22.0 10.6 48	
		Range		<0.011- 0.158		<0.20- 3.12	0.37- 1.83	8.6 42.8			<0.38- 2.32	<0.11 0.37		11.3- 21.4	
		\bar{x}^*	NA	0.068	ND	0.71	1.14	18.2	ND	ND	0.86	0.23	ND	17.3	
		sd		0.070		0.91	0.34	8.3			0.64	0.31		2.7	
		RSD%		102		127	30	45.4			74	133		16	
	Louisiana Platform Study														

1. Tillery, 1980

* Those samples at or below detection limit included as detection limit value.

ND = not determined

NA = data not available

Table 12
COMPARISON OF AVERAGE TRACE METAL CONCENTRATION IN STENOTOMUS CAPRINUS (LONGSPINE PORGY) MUSCLE TISSUE
($\mu\text{g/g}$ DRY WT) WITH OTHER GULF OF MEXICO STUDIES

			<u>Ba</u>	<u>Cd</u>	<u>Co</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Hg</u>	<u>Mn</u>	<u>Ni</u>	<u>Pb</u>	<u>Sr</u>	<u>Zn</u>
Buccaneer ¹	Summer 1978	\bar{x}	0.91	0.037	<0.30	0.58	1.82	22.3	0.027	1.81	1.63	0.14	32.5	16.1
		RSD% n=23	9	62	--	110	52	27	56	31	37	36	13	7
	1977	\bar{x}	ND	<0.01	ND	0.04	1.0	4.9	ND	ND	<0.07	<0.05	ND	12
		RSD% n=11		0		25	30	18			29	20		10
STOCS ²	1976	\bar{x}	ND	0.02	ND	0.03	0.9	4.6	ND	ND	0.10	0.05	ND	11
		RSD% n=9		50		33	22	41			30	80		34

1. *Stenotomus caprinus* substituted when no macrocrustacean samples were available.
2. Presley and Booth, 1979, Table 6.8, p 6-42.

There are no significant differences in trace metal burdens of sheepshead, spadefish or longspine porgy collected from the vicinity of the platforms with those from the well jacket (control).

To determine if there are significant seasonal differences in the trace metal concentrations in sheepshead and spadefish muscle tissues, an analysis of variance followed by a least significant difference means operation was performed on the data in Tables 10 and 11.

There were significant seasonal differences for all metals, except Cd, in sheepshead tissue (Table 10). There were significantly higher concentrations of Ba, Cr, Fe and Hg in the tissues during the spring. Winter season concentrations of Co, Cu, Pb, Mn, Ni and Zn were higher and, during the fall, Cu was also high. Sr concentrations were higher in the summer. Concentrations of Ba, Cr, Fe, and Hg were lower and more similar during the summer, fall and winter. Concentrations of Co, Mn, and Ni were lower and more similar during the summer, fall and spring. Summer and spring concentrations of Cu and Pb were lower and more similar while the fall, winter and spring concentrations of Sr are low and similar to each other. Zinc concentrations were generally lower in the fall, summer and spring seasons.

The Pb concentrations in the fall and the Mn concentrations in the spring were between the high concentrations in the winter and the lower concentrations in the spring (Pb) and fall (Mn). The Zn concentrations in the summer and spring are also in between the higher concentration in the winter and the lower concentration in the fall.

No seasonal differences were observed for Cd, Cr, Co, Cu and Zn in spadefish tissues (Table 11). However, there were significant seasonal differences for the remaining metals. Concentrations of Ba and Fe were highest in the spring. Lead concentrations

were higher in the winter. Concentrations of Mn and Hg were higher and more similar during the summer, winter and spring. Nickel tended to increase in concentration in the order of spring, fall, winter and summer with the spring and fall values being similar (and lower) and the fall, winter and summer being similar. The Ni concentrations in the fall are between the lower and higher concentrations.

Barium and Fe concentrations are lower and more similar in the summer, fall and winter. Lead concentrations tend to be lower and more similar in the summer, fall and spring. Fall concentrations of Mn and Hg are lower. Strontium concentrations increase in the order of fall, spring, winter and summer. The fall and spring Sr concentrations are more similar as are the spring and winter. Spring Sr concentrations are between the fall and winter concentrations in similarity.

To determine if bioaccumulation of any trace metals has occurred in sheepshead, spadefish or longspine porgy, a confidence interval was constructed around the summer mean values (Tables 10, 11 and 12) at a 95 percent confidence level, and the mean concentrations from the other studies tested to see if they were within this confidence interval. The summer data was selected for the sheepshead and spadefish since the time frame of collection closely matched the other study.

There were no significant differences in Cd, Pb and Zn concentrations in sheepshead tissue (Table 10) when compared to the Louisiana Platform data. There were significantly higher concentrations of Cr, Cu, Fe and Ni in the sheepshead from the Louisiana study.

Comparison of the spadefish data (Table 11) with the Louisiana study showed no significant difference in Ni and Zn concentrations. However, there were significant higher concentrations of the remaining metal (Cd, Cr, Cu, Fe and Pb) in the Louisiana samples.

All metals showed a significantly higher concentration in longspine porgy when compared to data from the STOCS study. This would suggest that bioaccumulation of trace metals has occurred in the longspine porgy from the Buccaneer oilfield. The production platform may be one source of these metals. However, since there were also high SPM trace metal concentrations during the summer, the possibility that this is a seasonal high rather than irreversible bioaccumulation cannot be ruled out. More information is needed on the seasonal variabilities of trace metals in this species.

The seasonal variations of trace metals in sheepshead and spadefish do not appear to be related to the platforms or satellite structures. Also, the seasonal highs do not correspond to the seasonal variations in the trace metal content of the sediments or SPM. There does not appear to be any bioaccumulation of trace metals in either sheepshead or spadefish muscle tissues.

Table 13 is a seasonal comparison of the trace metal concentrations in Trachypenaeus similis (sugar shrimp) by sampling location. Comparing the platform samples with the well jacket (control) samples show there are some higher concentrations of Cd. However, the high values at 296-B in the fall, 288-A in the winter and spring, and the well jacket (288-5) in the spring are due to one high sample in the groups analyzed. This is reflected in the high Relative Standard Deviation [$RSD(\%) = \frac{1 \text{ std. dev.}}{\text{mean}} \times 100$] for those samples with $n > 1$. One high sample at 288-A in the winter caused the high RSD(%) for Ni.

Other investigators have analyzed sugar shrimp from various areas of the Gulf. Table 14 is a comparison of our seasonal results with these other studies. Data from this table is a summary of the results presented in Table 13.

Concentrations of Cd are higher by a factor of one or two than what was reported in the MAFLA rig monitoring study (Presley and Booth, 1979) and the SPR monitoring program (Shokes, 1979).

Table 13
COMPARISON OF AVERAGE TRACE METAL CONCENTRATIONS IN TRACHYPENAEUS SIMILIS
(SUGAR SHRIMP) MUSCLE TISSUES BY SEASON AND LOCATION

			<u>Ba</u>	<u>Cd</u>	<u>Co</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Hg</u>	<u>Mn</u>	<u>Ni</u>	<u>Pb</u>	<u>Sr</u>	<u>Zn</u>
Fall	288-A	n=15(35)* X												
		RSD%	16	54	23	19	52	24	22	58	58	16	27	51
	296-B	n=5(40)* X	2.9	5.13	0.37	0.56	29.4	67.8	0.133	4.97	1.25	0.47	30	52
		RSD%	133	93	31	14	14	21	14	32	23	46	22	4
	288-5 Well Jacket	n=1(8)* X	9.4	0.22	<0.30	0.45	26.2	52.4	0.114	3.30	0.93	0.28	45	45
		RSD%	--	--	--	--	--	--	--	--	--	--	--	--
Winter	288-A	n=11(93)* X	1.6	0.862	0.53	0.52	25.6	48.8	0.123	4.91	1.66	0.33	39	46
		RSD%	21	232	49	28	28	19	9	78	117	40	26	4
	296-B	n=11(90)* X	1.8	0.378	0.84	0.67	28.1	50.5	0.136	3.03	2.91	0.65	50	50
		RSD%	25	89	68	88	9	19	17	16	70	125	20	5
	288-5 Well Jacket	n=1(8)* X	2.9	0.507	0.61	0.43	34.2	38.7	0.113	2.31	2.78	0.53	30	53
		RSD%	--	--	--	--	--	--	--	--	--	--	--	--
Spring	288-A	n=5(27)* X	4.4	1.36	0.39	1.07	34.6	66.1	0.155	5.09	0.45	0.24	24	54
		RSD%	7	173	23	79	20	15	16	28	20	27	21	3
	296-B	n=5(25)* X	4.1	0.207	0.36	1.11	33.3	53.7	0.160	2.68	0.74	0.22	23	54
		RSD%	10	22	25	9	14	22	22	19	57	32	11	3
	288-5 Well Jacket	n=1(6)* X	4.8	14.5	<0.30	0.51	28.0	82.9	0.118	4.55	<0.38	0.20	23	52
		RSD%	--	--	--	--	--	--	--	--	--	--	--	--

* n = number of pooled samples analyzed; () indicates number of individuals pooled.

Table 14
COMPARISON OF SEASONAL VARIATIONS IN AVERAGE TRACE METAL CONCENTRATIONS IN TRACHYPENAEUS SIMILIS
(SUGAR SHRIMP) MUSCLE TISSUE ($\mu\text{g/g}$ DRY WT) WITH OTHER GULF STUDIES

		<u>Cruise</u>	<u>Ba</u>	<u>Cd</u>	<u>Co</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Hg</u>	<u>Mn</u>	<u>Ni</u>	<u>Pb</u>	<u>Sr</u>	<u>Zn</u>
Buccaneer (<u>T. similis</u>)	Fall	\bar{x}	2.9	2.46	0.35	0.43	28.7	53.8	0.119	4.41	1.13	0.37	30	51
	n=11(83)*	RSD%	89	161	26	34	34	33	19	46	40	47	24	5
	Winter	\bar{x}	1.7	0.64	0.68	0.59	27.2	49.2	0.128	3.90	2.32	0.49	44	48
	n=23(191)*	RSD%	27	218	66	71	20	19	14	72	88	118	25	6
	Spring	\bar{x}	4.3	2.03	0.37	1.04	33.4	58.3	0.154	3.95	0.608	0.23	24	54
	n=11(58)*	RSD%	9	218	23	55	17	32	19	39	52	27	15	3
MAFLA Rig ¹ Monitoring (<u>T. similis</u>)	Before	\bar{x}	ND	0.03	ND	1.0	23	31	ND	ND	0.4	0.9	ND	ND
		RSD%		100		50	13	110			75	22		
	During	\bar{x}	ND	0.04	ND	0.7	25	57	ND	ND	0.5	0.6	ND	ND
		RSD%		150		57	12	42			80	67		
	After	\bar{x}	ND	0.03	ND	0.2	19	23	ND	ND	0.5	0.1	ND	ND
		RSD%		67		50	16	87			260	40		
SPR Brine Disposal Texoma Group Fall 1977-Winter 1978 ² (<u>Trachypenaeus</u> sp.)		\bar{x}	ND	0.017**	ND	0.131	16.8	65.8	ND	5.09	0.217	0.265	ND	60.2
		RSD%		--		24	19	42		24	44	42		6

1. Alexander, 1977, before, during and after refer to drilling operations; from Table 13, p 66.
2. Shokes, 1978, summary of data for West Hackberry Control II, Table 3.3-6, p 3-47.

* "n" is number of pooled samples; number in () is total individuals sampled.

** only one value given, others were "not detected".

ND = not determined.

The Ni concentrations during the summer and fall cruises were higher than what other investigators have reported, but the spring season data were similar.

These higher concentrations of Cd and Ni may be related to the platform structures; however, there were no abnormalities found in the sediment-Ni concentrations. Elimination of the high samples for Cd at the platforms would still give a mean concentration higher than that reported by other investigators. The high concentrations of Ba, Cd, and Pb in the sediments during the summer may have some relations to the fact that no shrimp samples were available around the platforms during this season.

D. Fouling Mat and Barnacles

Examination of fouling mat and barnacle samples for trace metals will provide information on what concentrations of these metals "grazing" fish are exposed to that inhabit the platform structures. It will also give some indication if there is metal contamination from the platform discharges. This will be reflected in an increase in certain metal concentrations near the source of discharge. Seasonal samples of fouling mat and barnacles were collected from the legs of platforms 288-A, 296-B, 296-B quarters, 296-B flare stack, and well jacket 288-5 at a water depth of eight meters. The 288-5 well jacket sample was used as a control.

Tables 15 and 16 summarize the seasonal trace metal concentrations in fouling mat and barnacles, respectively. One general observation of Table 15 for fouling mat is the low variation (RSD %) in the metal content considering the various flora and fauna that compose the fouling mat samples.

Comparison of the annual average concentrations of metals does not show any significant seasonal trends. However, there is a tendency for the well jacket (control) samples to have lower metal levels than the other samples through all seasons.

Table 15
SEASONAL VARIATION OF AVERAGE TRACE METAL CONCENTRATIONS ($\mu\text{g/g}$ DRY WT)
IN FOULING MAT (8 METER DEPTH)

Cruise	Sampling Location	Ba	Cd	Co	Cr	Cu	Fe*	Hg	Mn	Ni	Pb	Sr*	Zn
Summer	288-A	630	0.86	3.97	26.6	14.7	35.40	<0.008	318	39.0	18.8	2.2	167
	296-B**	675/698	<0.01/1.11	4.79/4.69	20.1/26.8	22.0/30.9	5.80/9.49	"	49/335	16.2/19.19	7/5.9	0.70/0.51	207/570
	296-B Quarters	570	0.82	1.53	3.79	10.6	0.42	"	109	8.8	1.9	0.7	40
	296-B Flare Stack	731	2.14	1.22	2.99	71.0	0.47	"	110	10.2	0.9	1.9	33
	288-5 Well Jacket	1190	0.56	2.55	9.43	16.1	1.79	"	302	19.4	7.6	3.1	99
	\bar{x}	749	0.92	3.13	15.0	27.6	3.59	<0.008	304	18.8	7.5	1.5	186
	RSD% n=6	30	77	50	73	81	99	--	65	58	87	70	108
Fall	288-A	873	2.27	3.36	24.6	14.1	5.93	<0.008	274	16.7	15.3	1.7	104
	296-B**	776/870	2.45/3.47	2.25/2.96	14.6/559	9.4/60	4.19/10.0	"	64/157	13.9/32.2	3.3/4.9	0.37/0.25	231/104
	296-B Quarters	792	2.66	1.73	9.68	8.3	2.11	"	143	13.5	2.7	0.4	51
	296-B Flare Stack	1040	2.36	2.14	10.3	11.9	2.53	"	96	12.0	3.1	0.3	54
	288-5 Well Jacket	1074	1.63	3.88	11.7	7.5	3.28	"	128	14.4	2.4	0.7	44
	\bar{x}	904	2.47	2.72	105	18.6	4.68	<0.008	160	17.1	5.3	0.7	98
	RSD% n=6	14	24	30	21	111	63	--	38	44	94	89	72
Winter	288-A	192	2.00	3.15	5.72	11.7	3.54	<0.008	288	6.5	8.62	2.6	137
	296-B**	473/152	1.52/2.47	4.79/4.45	25.6/10.6	12.4/13.1	7.29/5.65	"	484/246	12.1/8.7	15.3/11.4	4.0/3.3	92/68
	296-B Quarters	222	1.02	3.12	8.23	11.2	3.52	"	191	7.3	8.75	2.2	65
	296-B Flare Stack	192	3.61	3.36	6.72	11.3	4.32	"	226	8.2	9.26	1.4	60
	288-5 Well Jacket	122	0.58	2.46	6.87	11.9	3.72	"	195	7.2	10.5	2.6	61
	\bar{x}	226	1.87	3.56	10.6	11.9	4.67	<0.008	272	8.3	10.6	2.7	81
	RSD% n=6	56	58	25	71	6	32	--	41	24	24	33	37
Spring	288-A	276	1.41	2.58	11.2	13.1	3.59	<0.008	255	5.9	6.04	3.1	102
	296-B**	151/382	1.65/1.03	4.71/8.20	10.5/12.1	13.2/14.4	4.47/6.59	"	373/503	7.8/10.8	3.9/8.5	4.2/4.0	107/73
	296-B Quarters	232	4.14	4.49	10.0	14.7	5.32	"	330	9.2	10.5	1.3	53
	296-B Flare Stack	512	3.15	2.49	8.9	15.7	3.93	"	285	7.5	9.10	1.7	55
	288-5 Well Jacket	99	0.96	2.46	5.6	11.8	2.73	"	262	5.9	2.43	3.7	63
	\bar{x}	275	2.06	4.16	9.7	13.8	4.44	<0.008	335	7.9	6.75	3.0	76
	RSD% n=6	55	63	54	24	10	31	--	28	24	47	41	31

* concentration in mg/g

** duplicate samples

Table 16
SEASONAL VARIATIONS OF AVERAGE TRACE METAL CONCENTRATIONS ($\mu\text{g/g}$ DRY WT) IN BARNACLE
(PREDOMINANTLY, BALANUS TINTINNABULUM) SOFT TISSUE

Cruise	Sampling Location	Ba	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sr	Zn
Summer	288-A	5.4	12.5	0.92	2.2	22.2	107	0.020	18.0	25.3	0.71	122	449
	296-B*	3.6/6.0	13.5/9.8	2.39/0.95	1.9/1.3	17.6/16.3	100/99	0.012/0.028	15.5/15.0	8.7/9.2	0.17/0.69	92/93	417/346
	296-B Quarters	6.6	10.3	1.0	2.2	17.7	120	0.014	17.0	4.5	0.51	153	369
	296-B Flare Stack	6.5	9.9	0.82	1.5	17.1	108	0.013	17.0	6.9	0.42	185	332
	288-5 Well Jacket	4.2	8.8	1.0	1.7	17.9	122	0.029	16.5	4.7	0.37	105	341
	\bar{x}	5.4	10.8	1.18	1.8	18.1	109	0.019	16.5	9.9	0.48	125	376
	RSD% n=6	23	17	51	21	11	9	42	7	79	43	30	13
Fall	288-A	9.4	11.3	1.4	2.7	13.4	437	<0.008	24.5	10.2	1.57	109	341
	296-B*	12.0/10.6	12.0/11.9	1.1/1.6	2.9/2.7	14.5/17.4	468/449	0.015/0.012	24.5/25.0	8.2/10.0	1.47/0.60	189/222	342/339
	296-B Quarters	6.8	11.1	1.8	1.8	13.8	333	0.011	21.5	8.1	0.43	103	243
	296-B Flare Stack	8.5	14.1	1.2	1.6	15.0	447	0.021	24.0	10.8	2.20	144	258
	288-5 Well Jacket	4.3	7.4	0.7	1.4	7.3	259	0.026	16.5	8.6	0.67	80	136
	\bar{x}	8.6	11.3	1.3	2.2	13.6	399	0.016	22.7	9.3	1.16	141	277
	RSD% n=6	32	19	30	30	25	21	44	14	13	60	39	30
Winter	288-A	6.5	25.0	0.92	8.1	27.8	259	0.035	22.6	5.6	0.33	233	661
	296-B*	3.9/4.9	23.6/21.5	0.55/0.50	2.3/9.3	23.1/24.3	157/155	0.032/0.034	8.84/9.97	4.8/10.0	1.92/0.43	115/138	588/415
	296-B Quarters	6.2	23.6	0.60	2.5	27.1	194	0.040	14.1	3.2	0.39	236	511
	296-B Flare Stack	8.6	28.5	0.33	1.8	32.7	173	0.041	12.3	1.7	0.86	382	469
	288-5 Well Jacket	8.7	18.1	<0.30	4.7	17.4	168	0.039	12.7	2.1	0.81	103	403
	\bar{x}	6.5	23.4	0.53	4.8	25.4	184	0.037	13.4	4.5	0.79	201	508
	RSD% n=6	30	15	42	68	20	21	11	36	68	76	53	20
Spring	288-A	3.8	14.2	1.30	1.3	11.8	82	0.016	15.3	4.4	<0.11	107	329
	296-B*	4.6/4.2	14.0/15.7	0.92/0.35	0.9/1.4	13.2/16.5	121/78	0.010/0.029	11.7/11.1	4.8/5.9	<0.11/0.21	2560/951	282/207
	296-B Quarters	7.2	11.6	4.6	2.1	13.2	107	0.017	11.4	2.2	0.30	258	255
	296-B Flare Stack	3.1	13.6	0.46	0.8	16.7	87	0.017	12.9	6.0	<0.11	114	333
	288-5 Well Jacket	7.8	9.8	0.30	0.9	14.0	114	0.016	16.4	2.1	0.20	265	266
	\bar{x}	5.1	13.1	1.3	1.2	14.3	98	0.018	13.1	4.2	0.17	709	279
	RSD% n=6	38	16	125	40	14	19	33	17	40	45	135	17

* duplicate samples

Table 16 for barnacles does not show any significant seasonal trends. There appears to be slightly lower values for the well jacket (control) samples but analytical variability makes this difficult to determine. The predominant species sampled was Balanus tintinnabulum.

There is no indication of higher concentrations of Ba and Sr from the produced brine discharges accumulating in either the fouling mat or barnacle samples.

IV. CONCLUSIONS

Concentrations gradients of Ba, Cd, Cr, Cu, Mn, Pb, Sr, and Zn in surficial sediments at platform structures 288-A and 296-B are not related to the hydrated iron fraction of the sediments or the sediment grain size. This suggests these metals have an input that is related to the platform structures or petroleum production activities.

There are seasonal variation in the concentration and distribution of these metals in the sediments near the platform structures. Generally, the summer and fall seasons have higher and more variable concentrations while the winter and spring are lower and less variable.

There is a significant accumulation of Cr, Hg, Pb, Sr and Zn in the sediments around the platform structures.

Suspended particulate matter trace metal concentrations are highly variable with the higher concentrations present in the summer. Due to the variability, SPM trace metal concentrations cannot be related to the platform discharges. Comparison of normalized SPM and surficial sediment data suggest resuspended sediments as a source of Pb during the summer, fall and winter, and of Sr in the spring.

Produced brine samples contain higher concentrations of Ba, Cr, Fe, Mn and Sr relative to sea water. The average concentration of Ba was 1.39 ppm. This is similar to last year's reported concentration. The average Sr concentration (70.7 ppm) is about twice last year's average concentration.

There are significant seasonal variations in all metals except Cd in Archosargus probatocephalus (sheepshead) and Ba, Fe, Pb, Mn, Hg, Ni, Sr and Zn in Chaetodipterus faber (spadefish) tissues. Seasonal variations in heavy metal concentrations in

sheepshead and spadefish are not necessarily related to the platform structures. Bioaccumulations of Cd, Cr, Cu, Fe, Ni, Pb and Zn has not occurred in either sheepshead or spadefish.

Comparison of the heavy metal concentrations from Stenostomus caprinus (longspine porgy) with data from other studies indicate bioaccumulation of Cd, Cr, Cu, Fe, Ni, Pb and Zn has occurred. Lack of sensitivity for Cr and Ni may cause a bias towards higher mean concentrations for these metals. The higher metal concentrations in the longspine porgy may be related to the higher (and more variable) metal concentration in the surficial sediments near the platforms during the summer. Insufficient data on the seasonal variation of these metals in longspine porgy prevents confirmation of irreversible bioaccumulation.

There were higher concentrations of Cd in Trachypenaeus similis (sugar shrimp) than what other investigators have found in this species. Higher Ni concentrations were found in the fall and winter but had returned to normal by spring.

No significant trends or increases were noted for heavy metal concentrations in fouling mat or barnacles in any season.

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APPENDIX

Figures

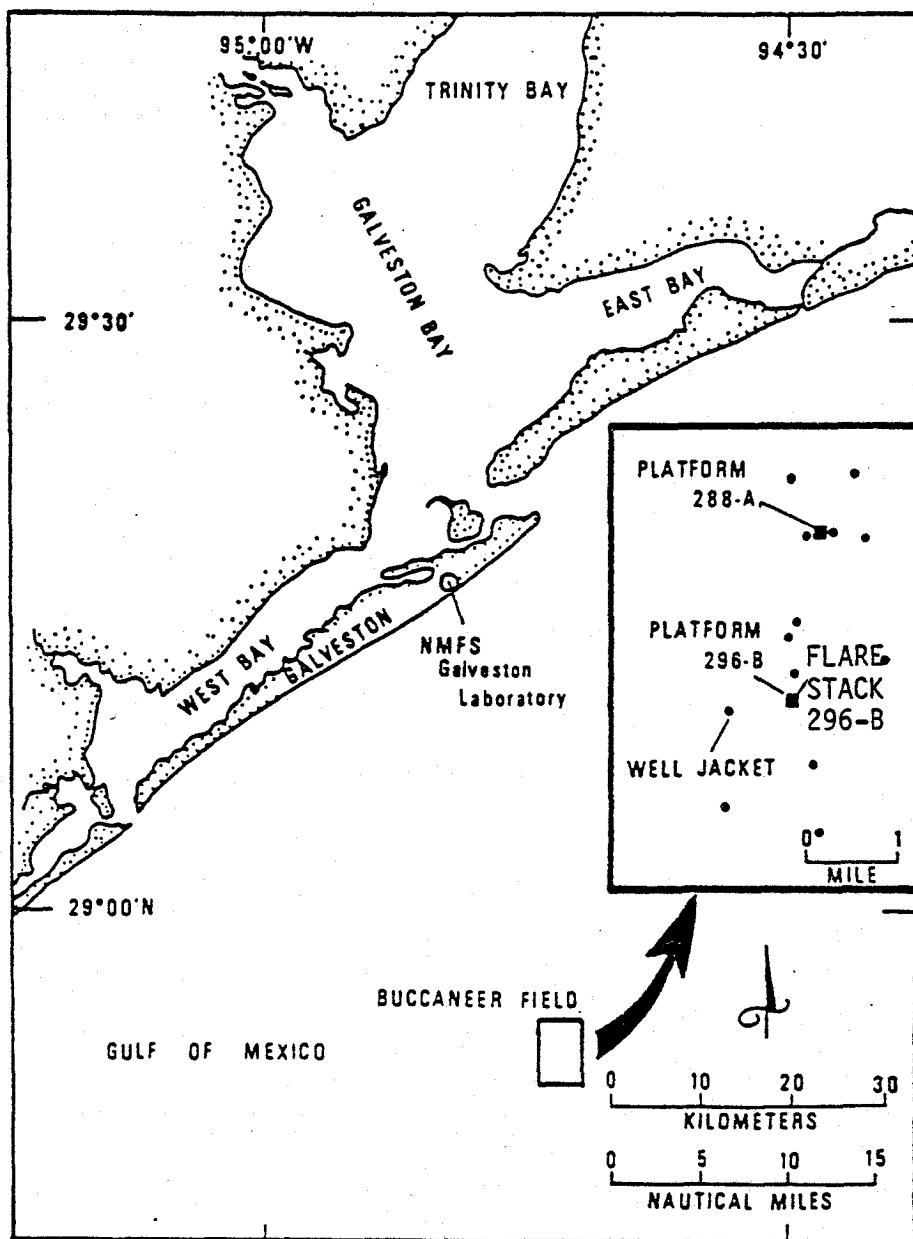


Figure 1. Map of Study Area

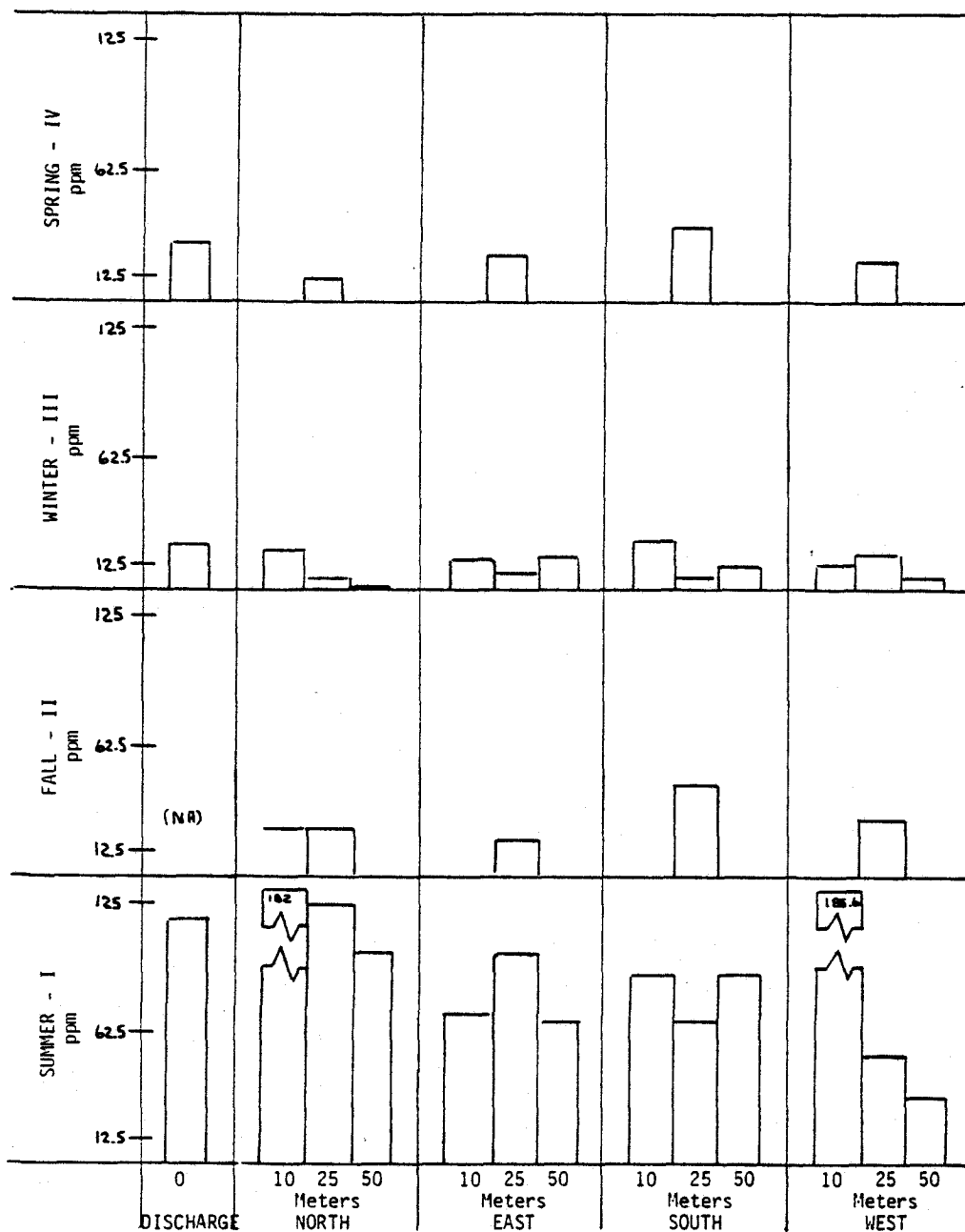


Figure 2. Temporal and Spacial Variation of Ba in Surficial Sediments at Platform 288-A

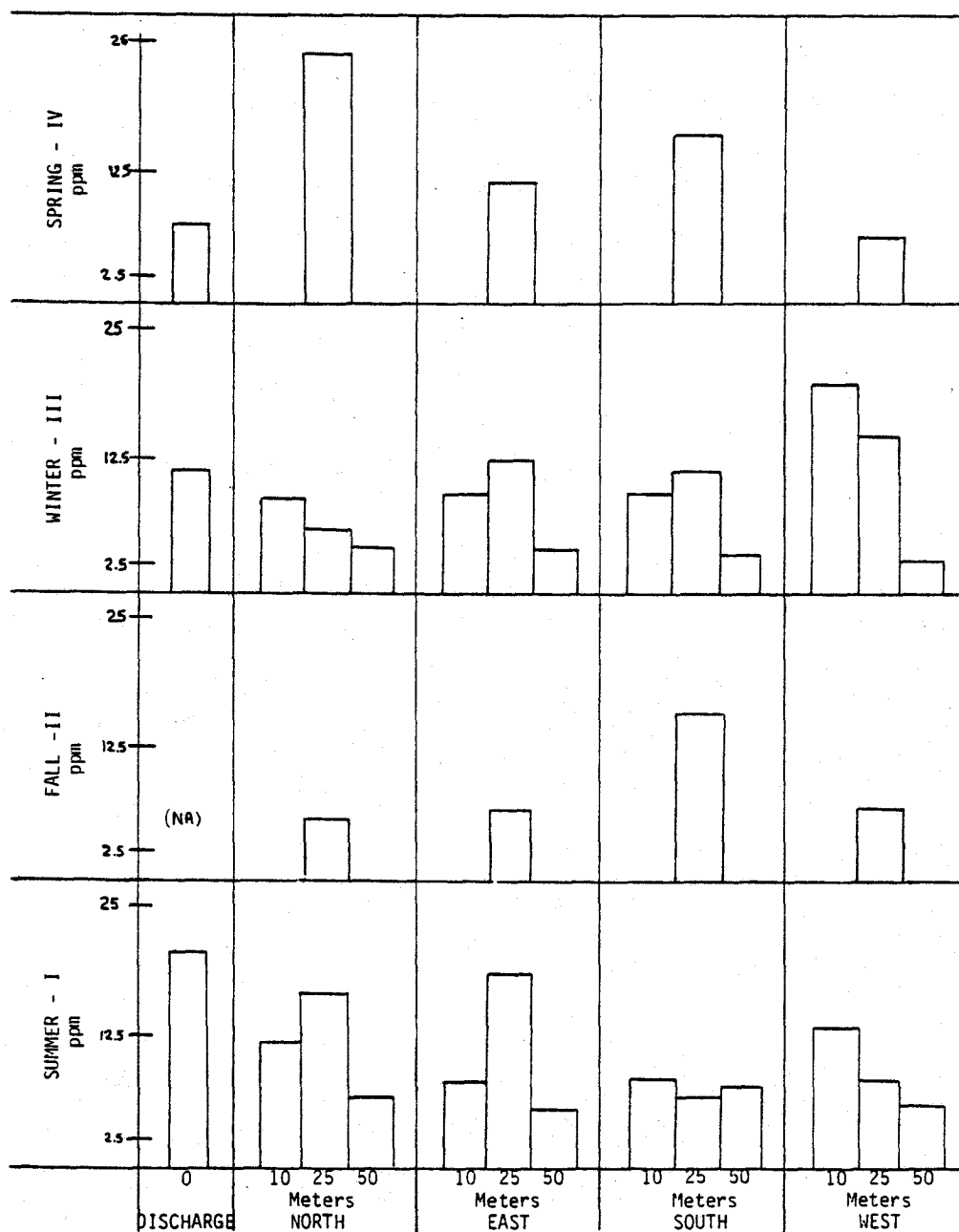


Figure 3. Temporal and Spacial Variation of Cd in Surficial Sediments at Platform 288-A

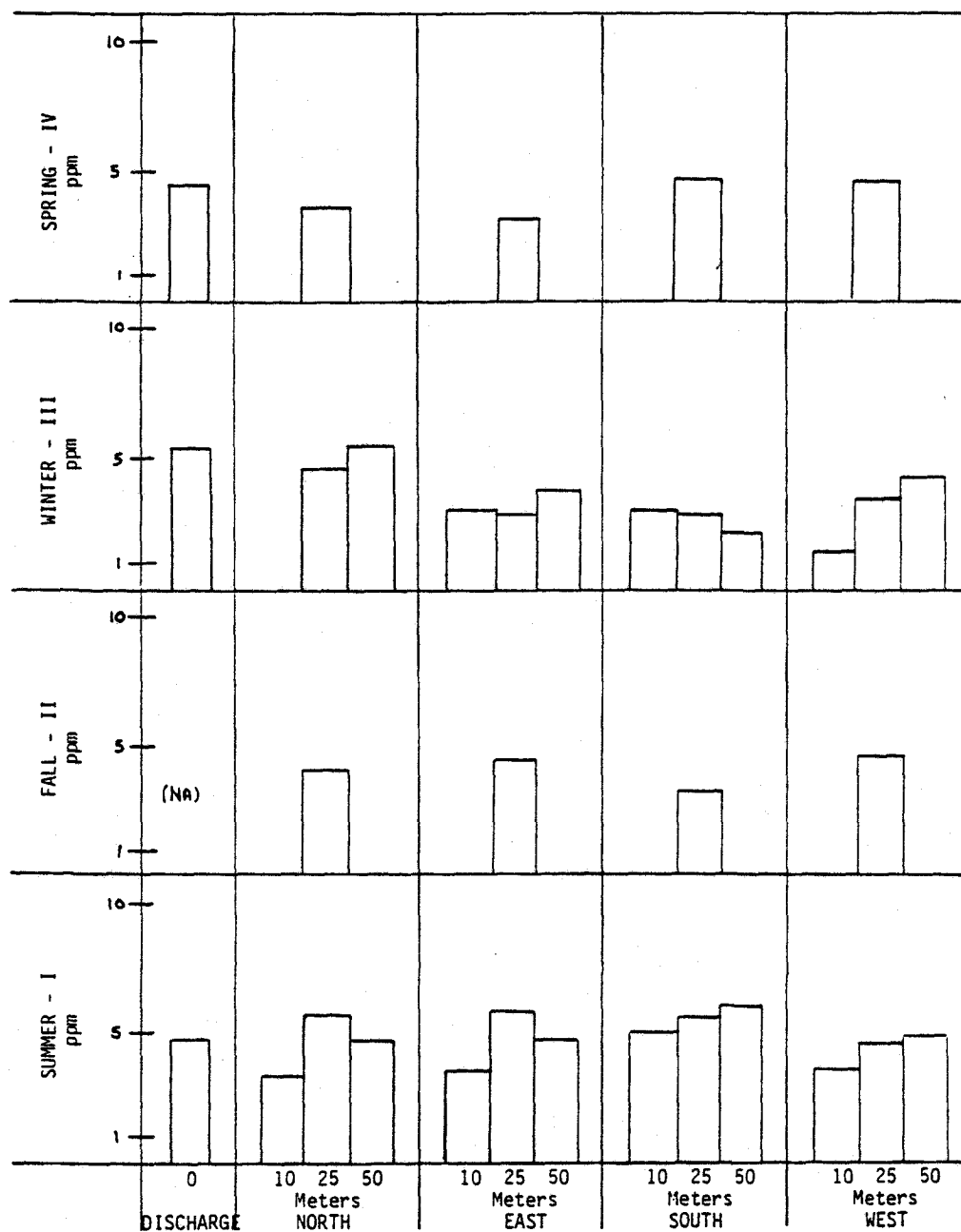


Figure 4. Temporal and Spacial Variation of Co in Surficial Sediments at Platform 288-A

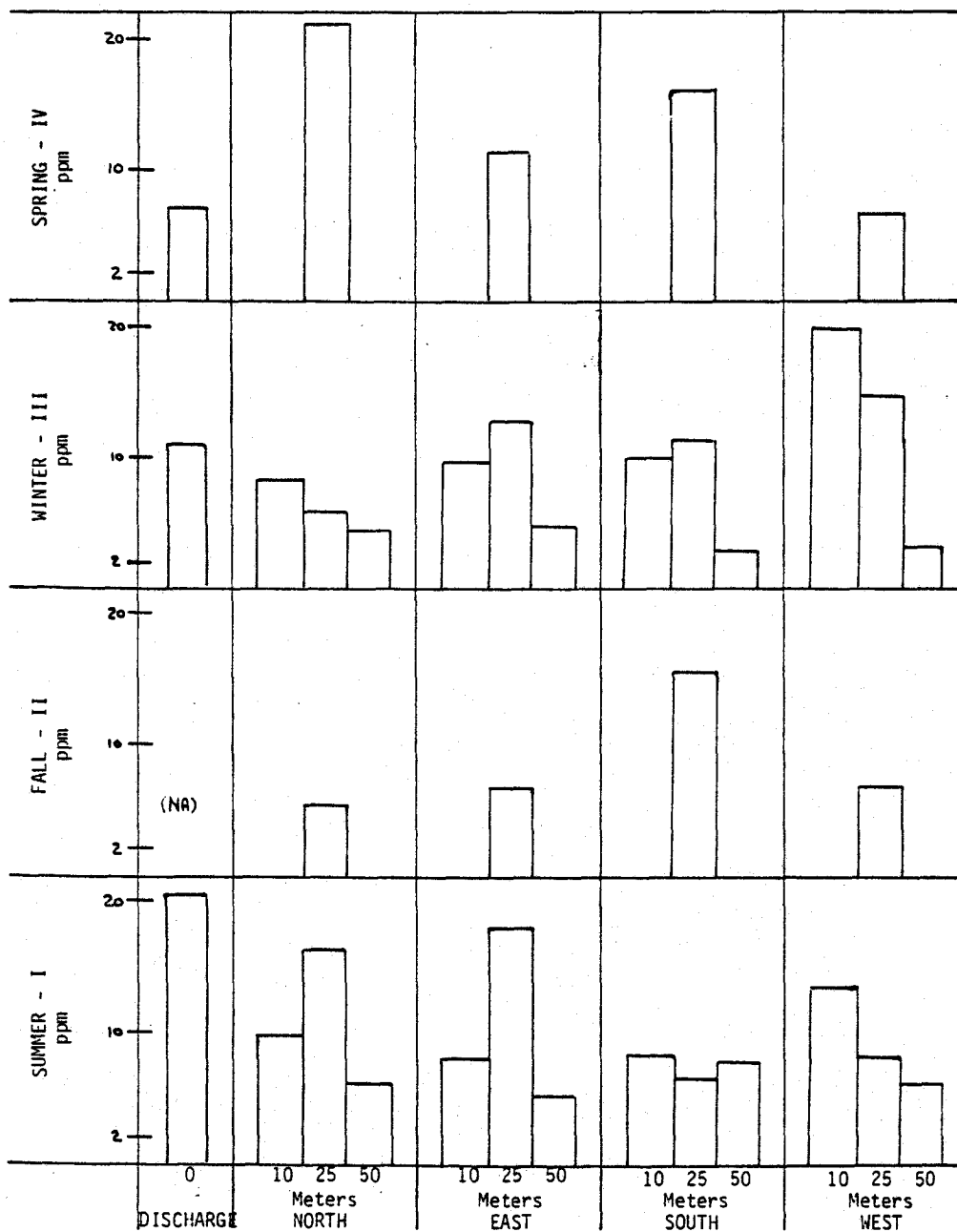


Figure 5. Temporal and Spacial Variation of Cr in Surficial Sediments at Platform 288-A

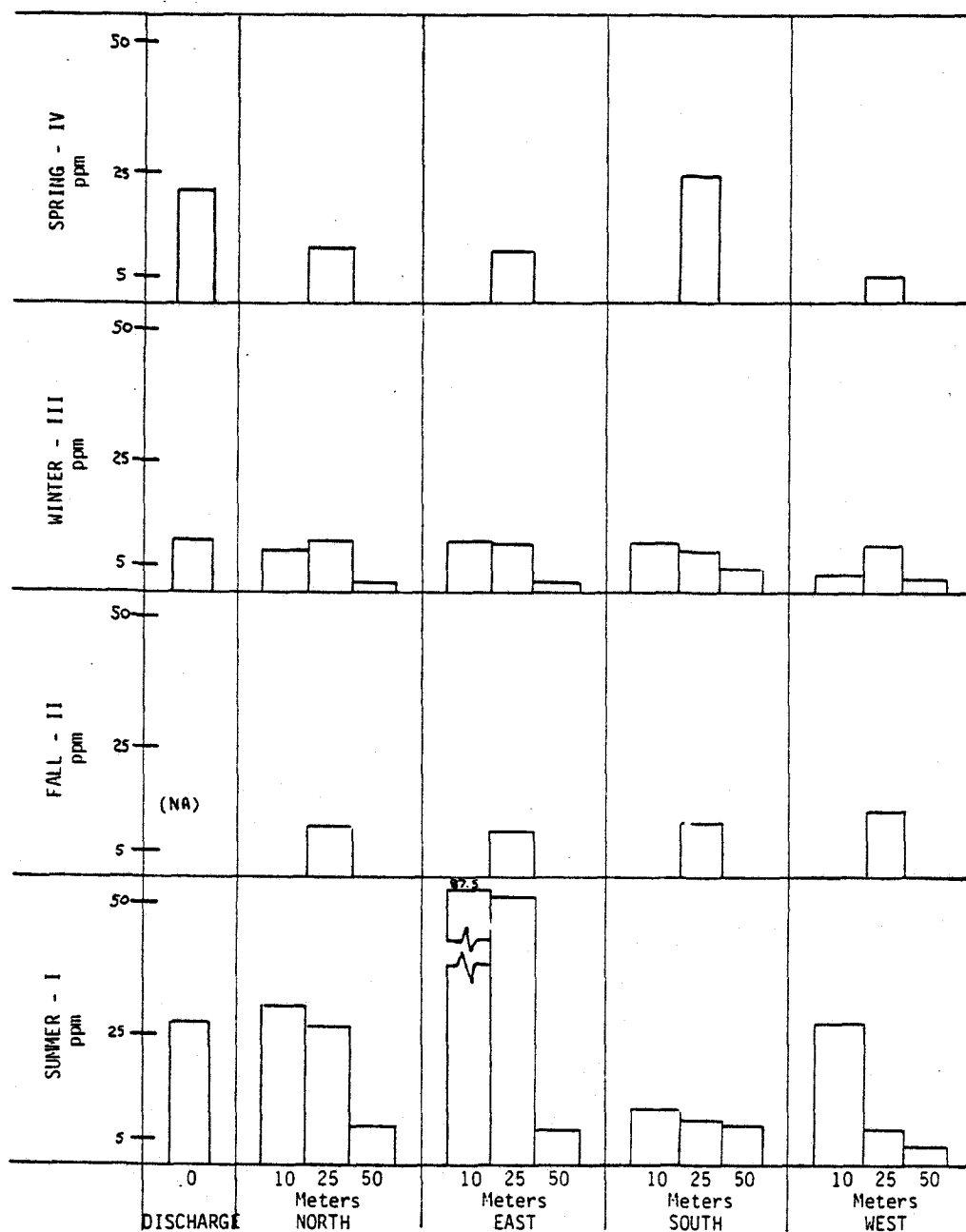


Figure 6. Temporal and Spatial Variation of Cu in Surficial Sediments at Platform 288-A

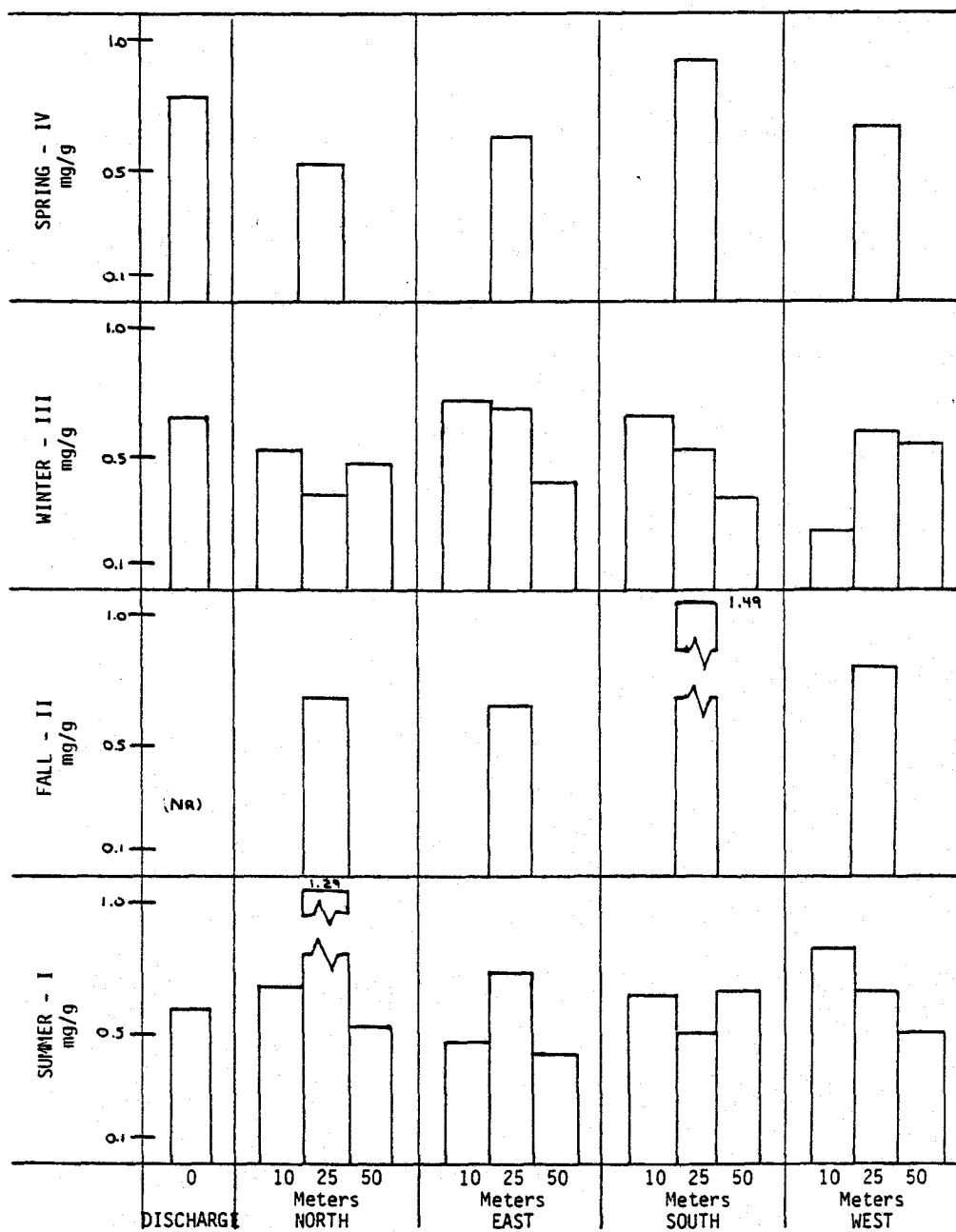


Figure 7. Temporal and Spacial Variation of Fe in Surficial Sediments at Platform 288-A

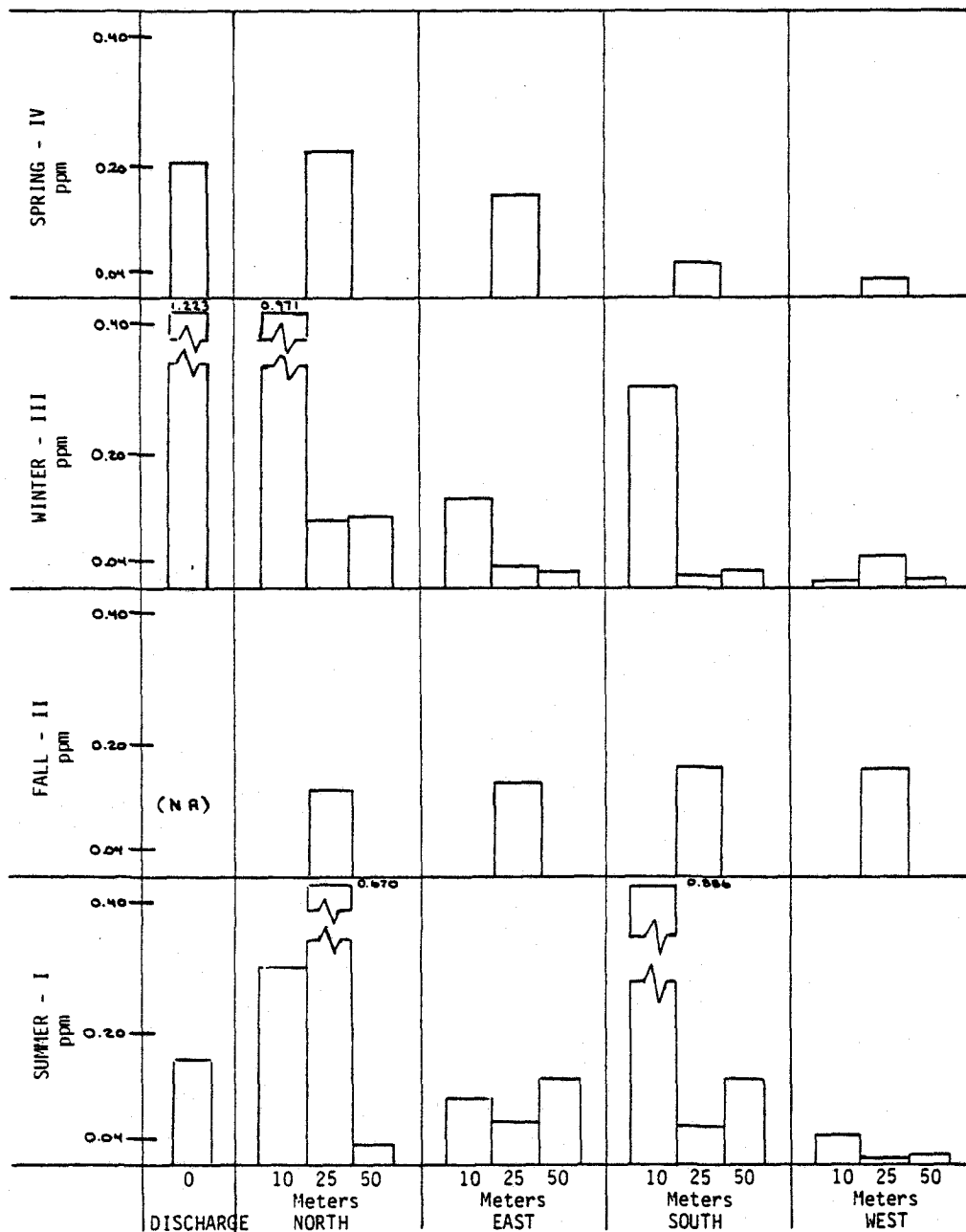


Figure 8. Temporal and Spacial Variation of Hg in Surficial Sediments at Platform 288-A

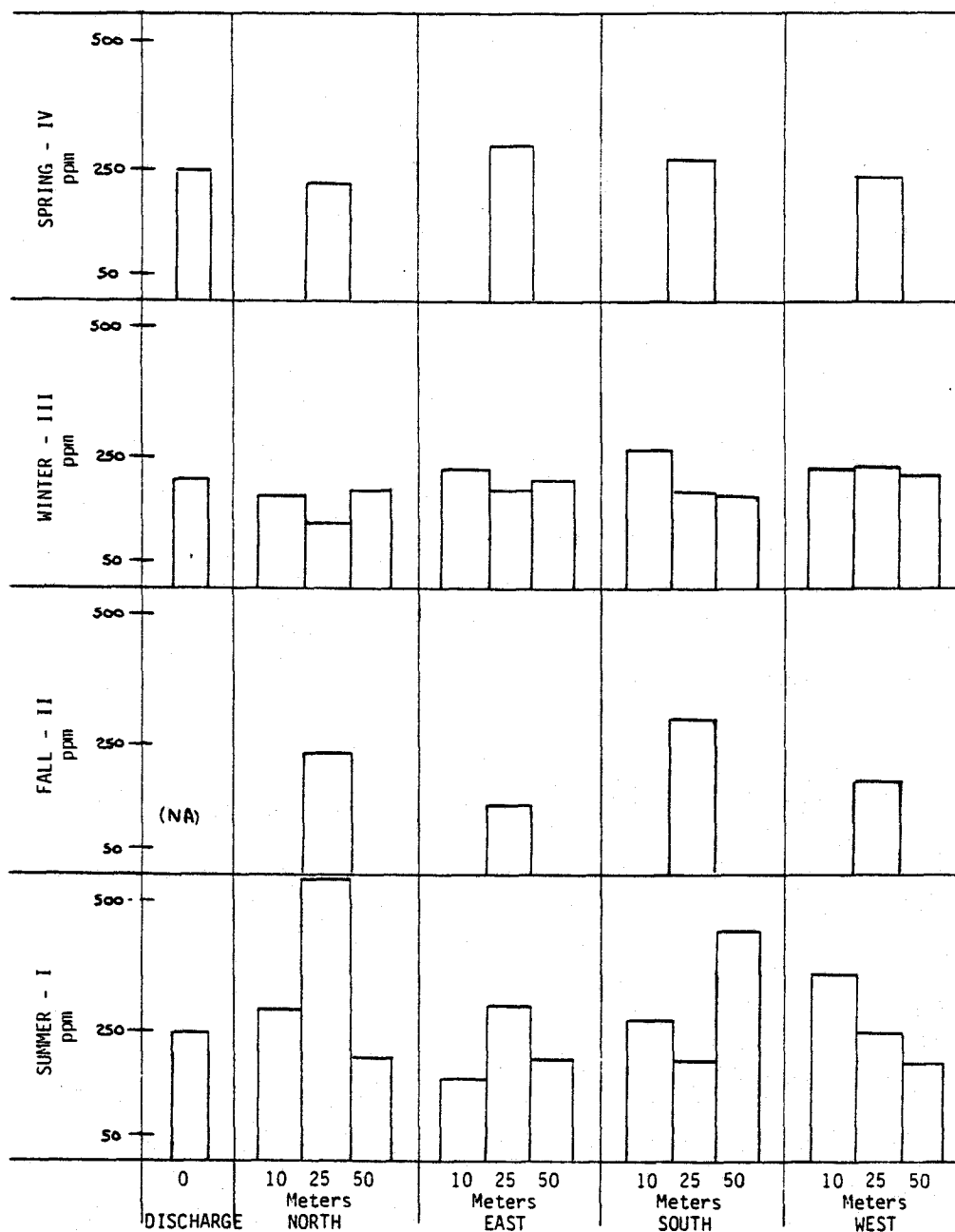


Figure 9. Temporal and Spatial Variation of Mn in Surficial Sediments at Platform 288-A

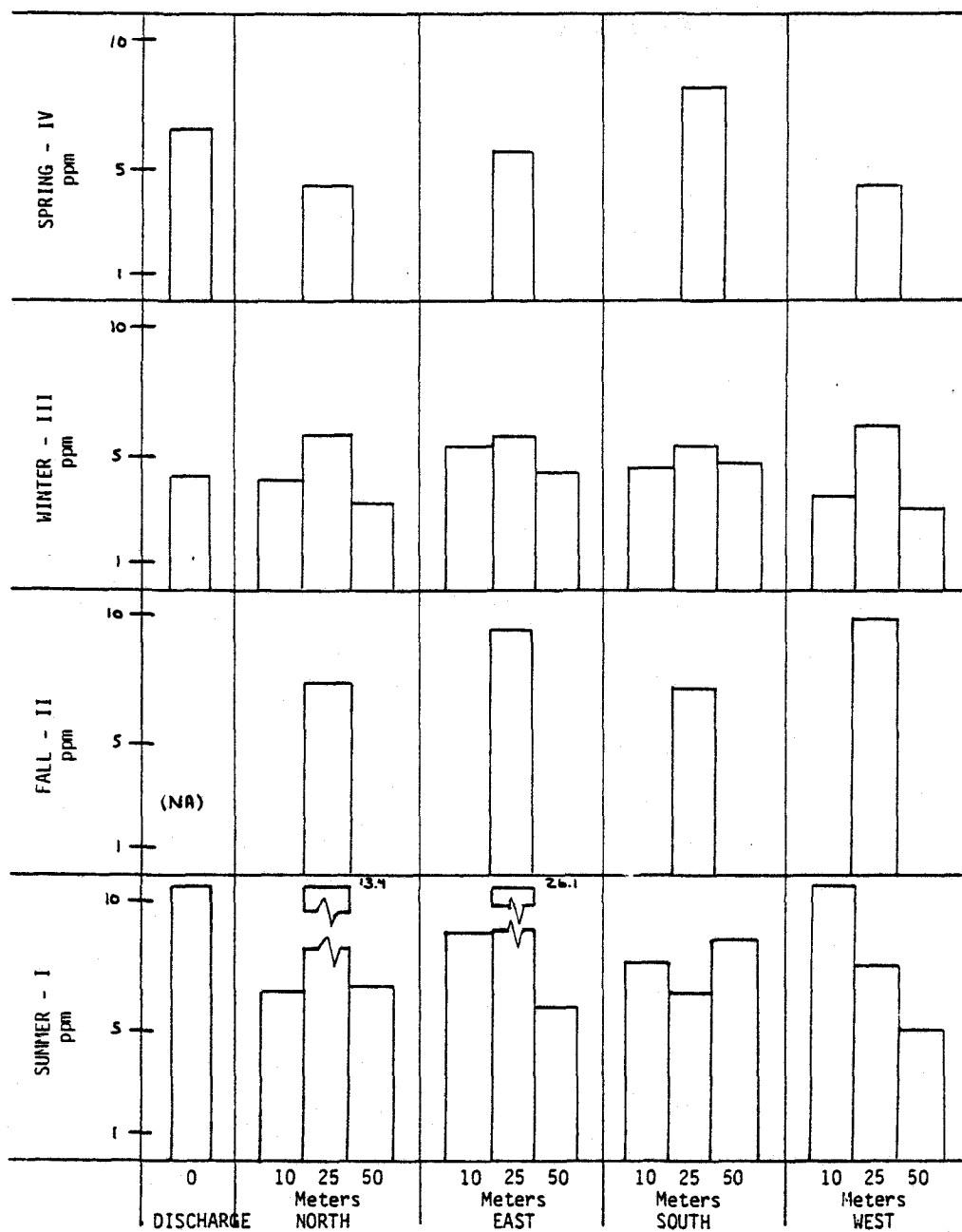


Figure 10. Temporal and Spatial Variation of Ni in Surficial Sediments at Platform 288-A

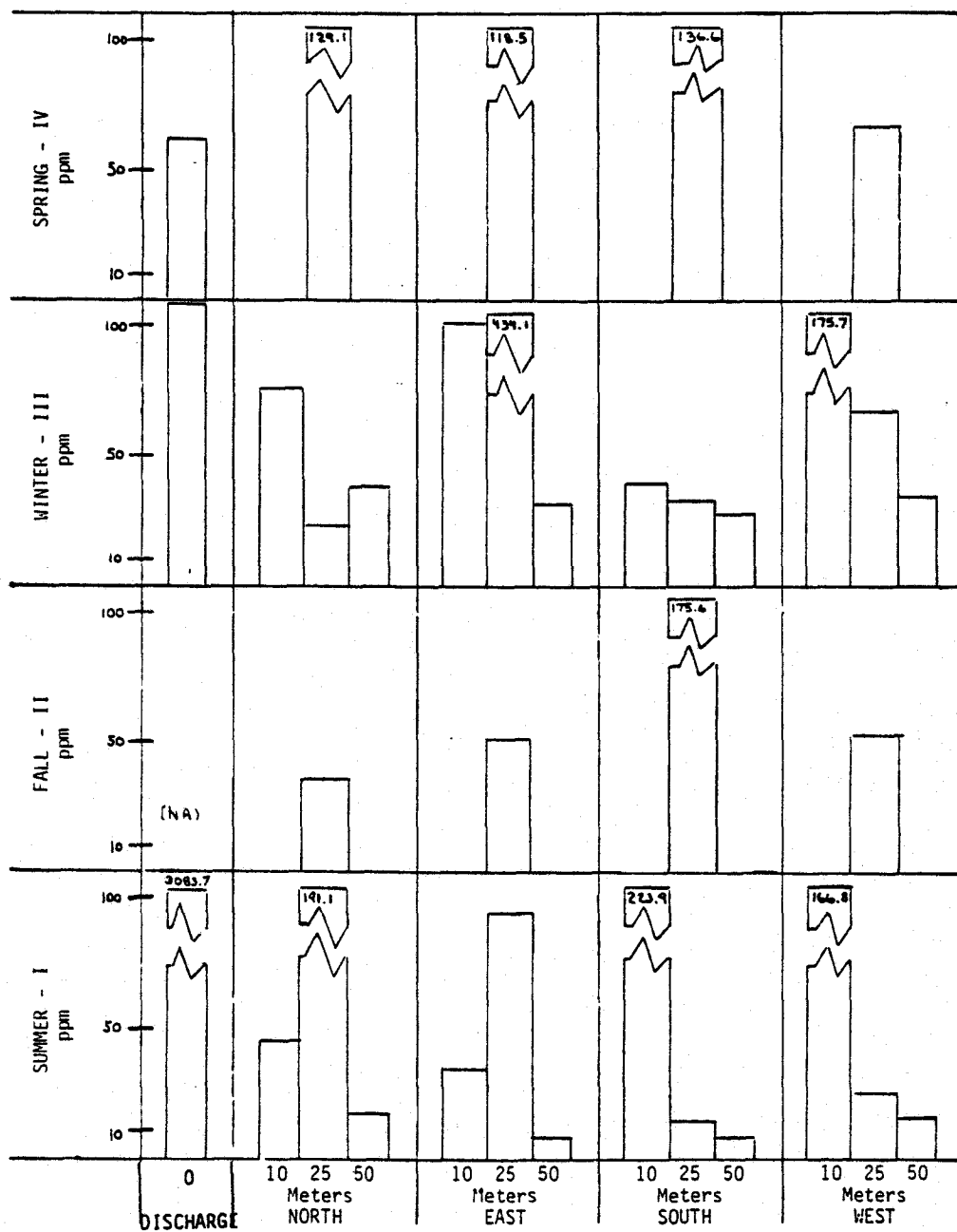


Figure 11. Temporal and Spatial Variation of Pb in Surficial Sediments at Platform 288-A

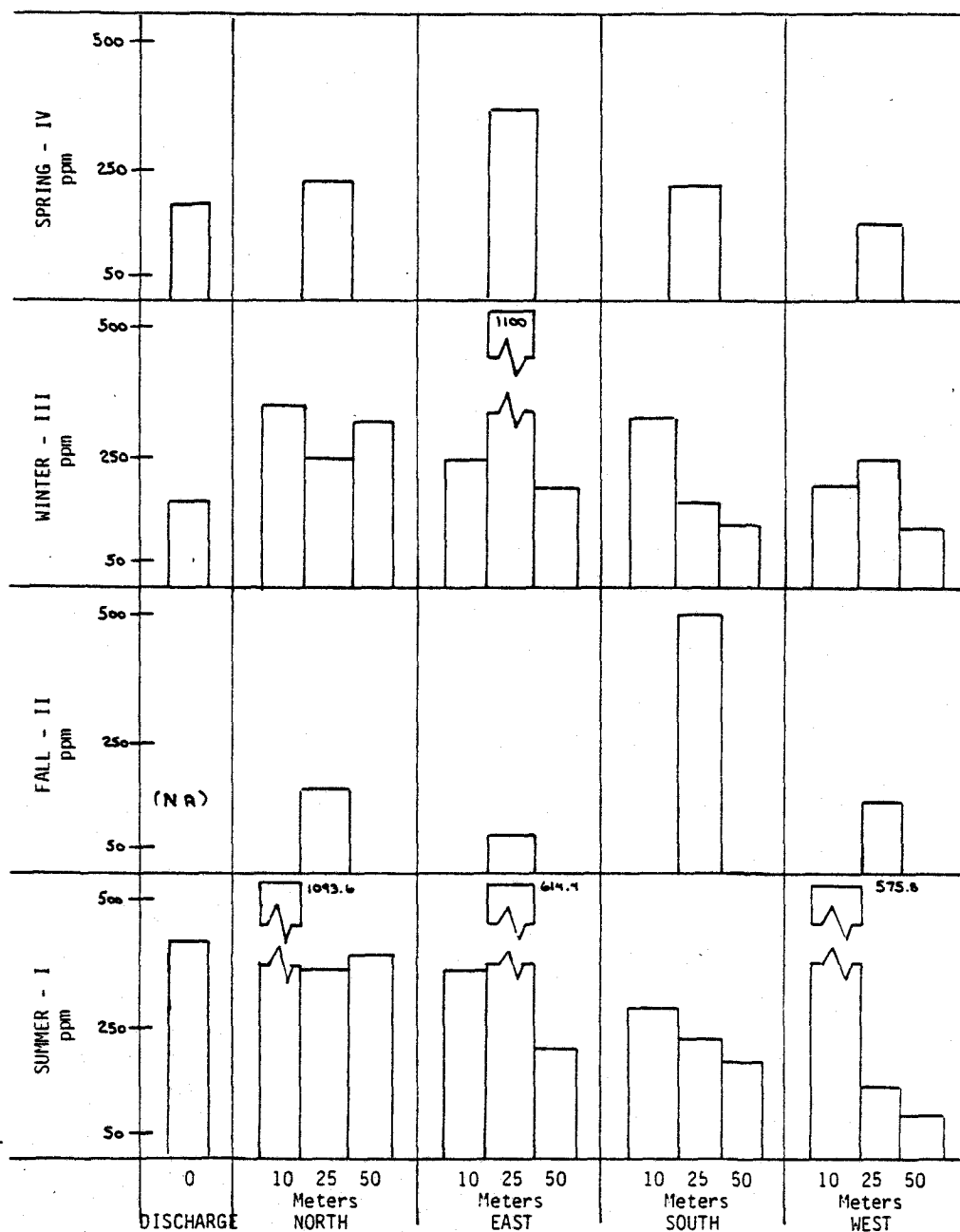


Figure 12. Temporal and Spatial Variation of Sr in Surficial Sediments at Platform 288-A

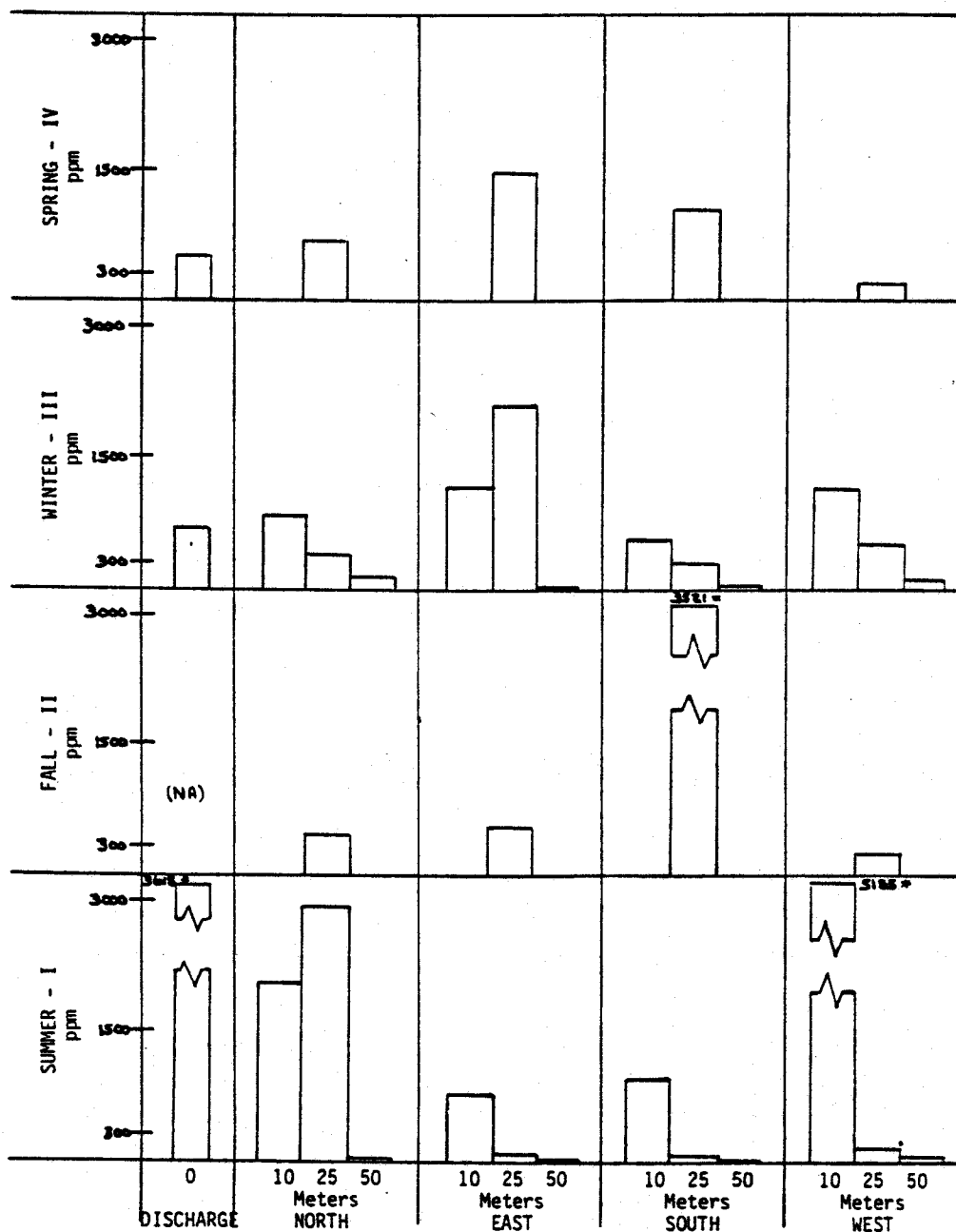


Figure 13. Temporal and Spatial Variation of Zn in Surficial Sediments at Platform 288-A

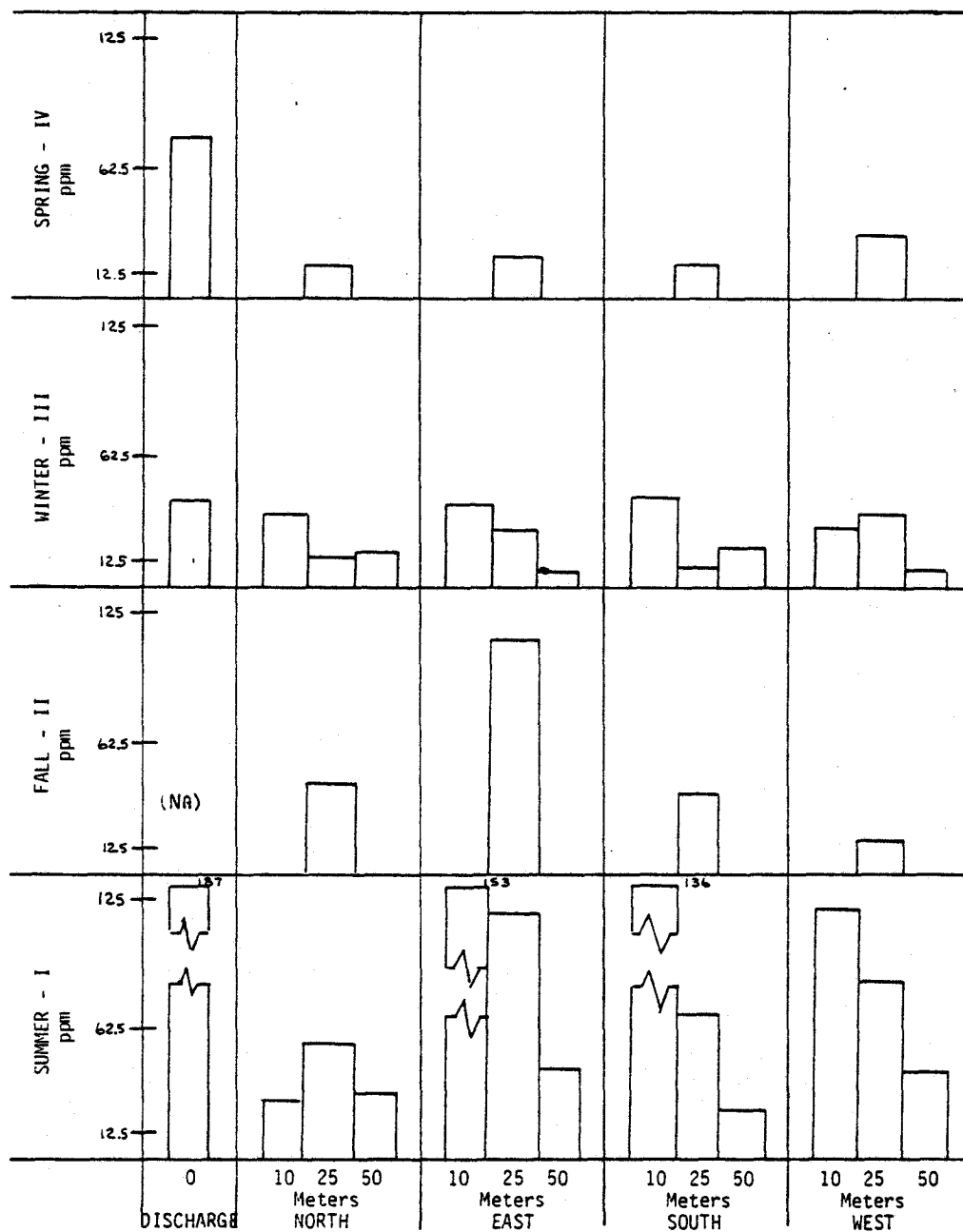


Figure 14. Temporal and Spacial Variation of Ba in Surficial Sediments at Platform 296-B

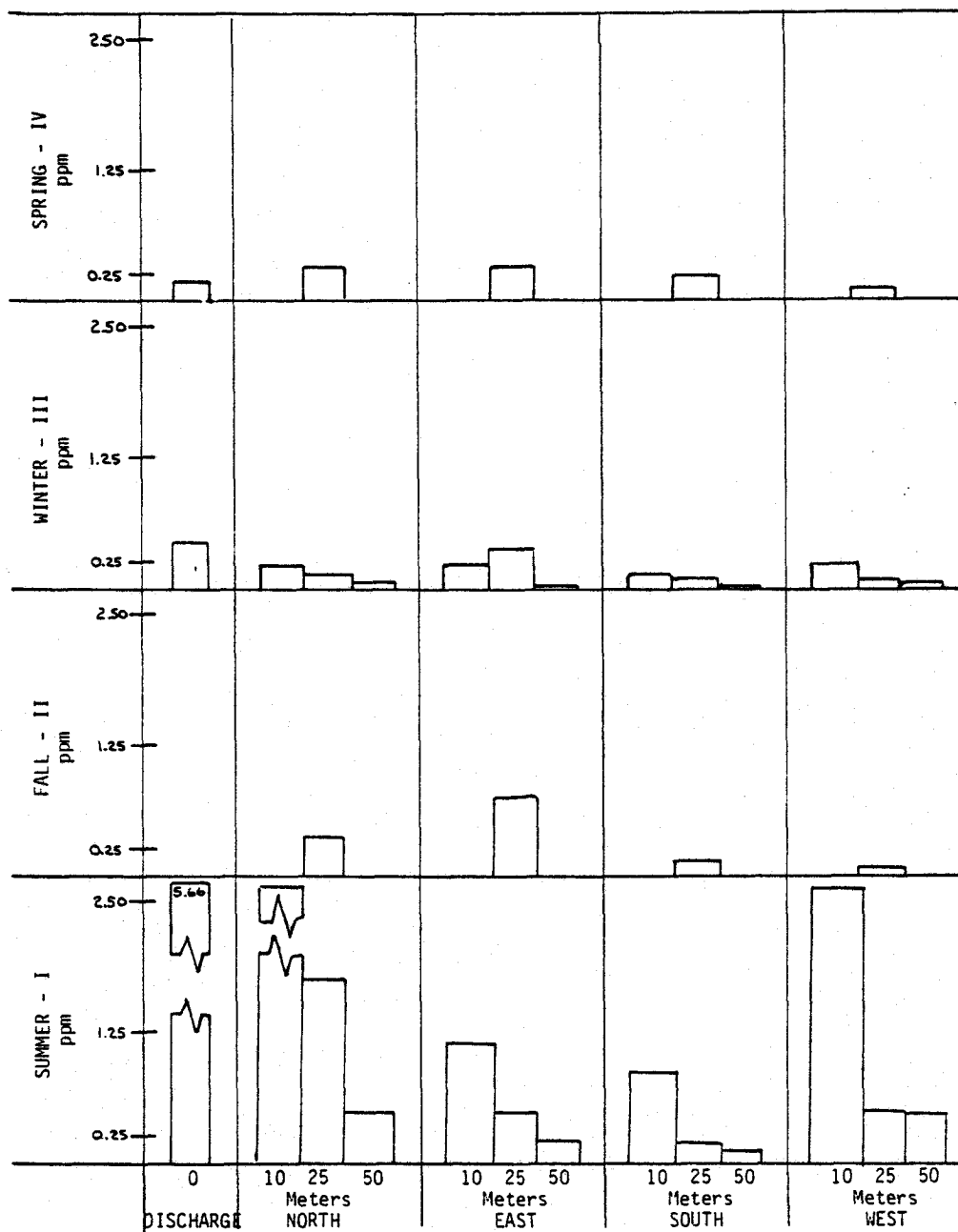


Figure 15. Temporal and Spacial Variation of Cd in Surficial Sediments at Platform 296-B

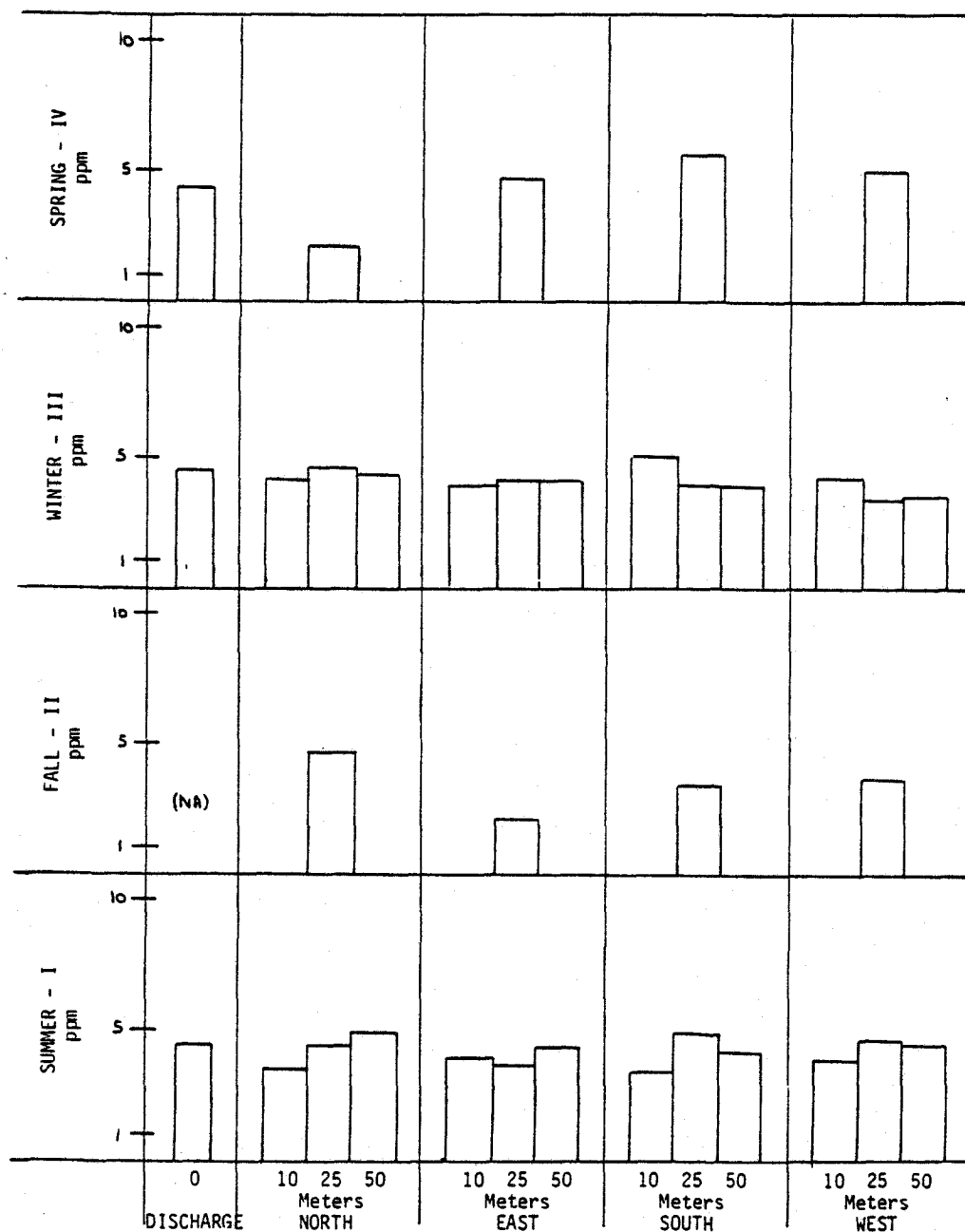


Figure 16. Temporal and Spatial Variation of Co in Surficial Sediments at Platform 296-B

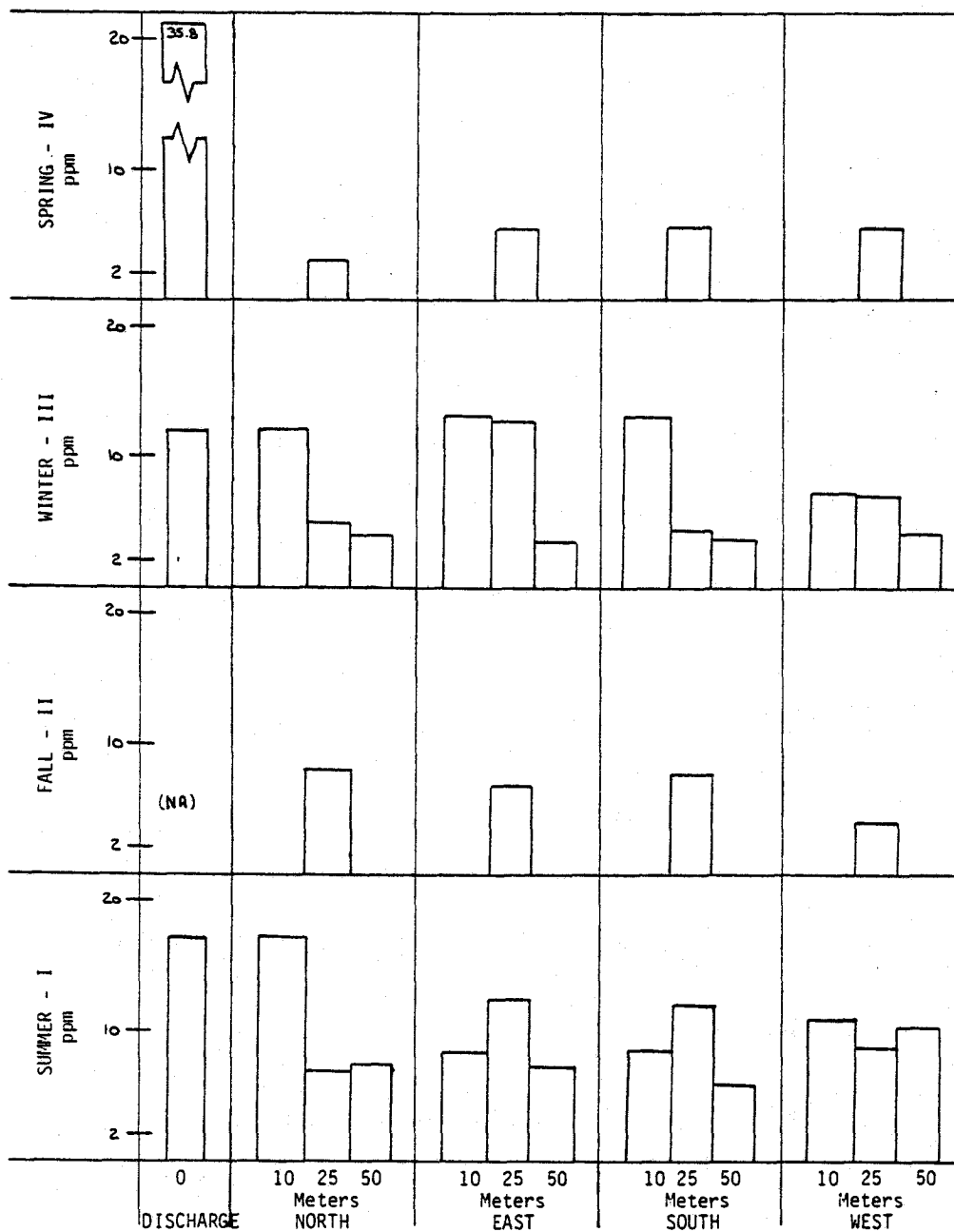


Figure 17. Temporal and Spacial Variation of Cr in Surficial Sediments at Platform 296-B

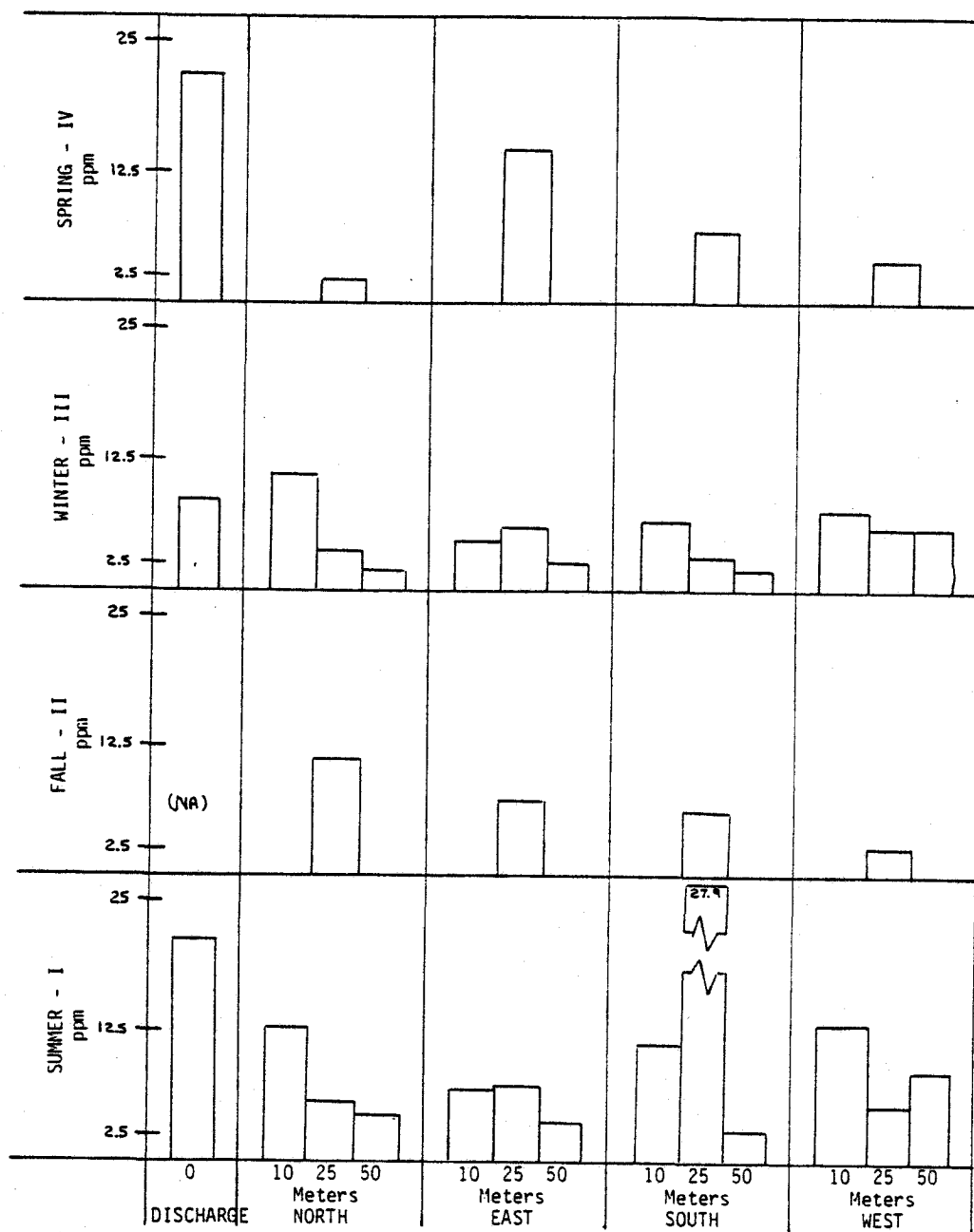


Figure 18. Temporal and Spacial Variation of Cu in Surficial Sediments at Platform 296-B

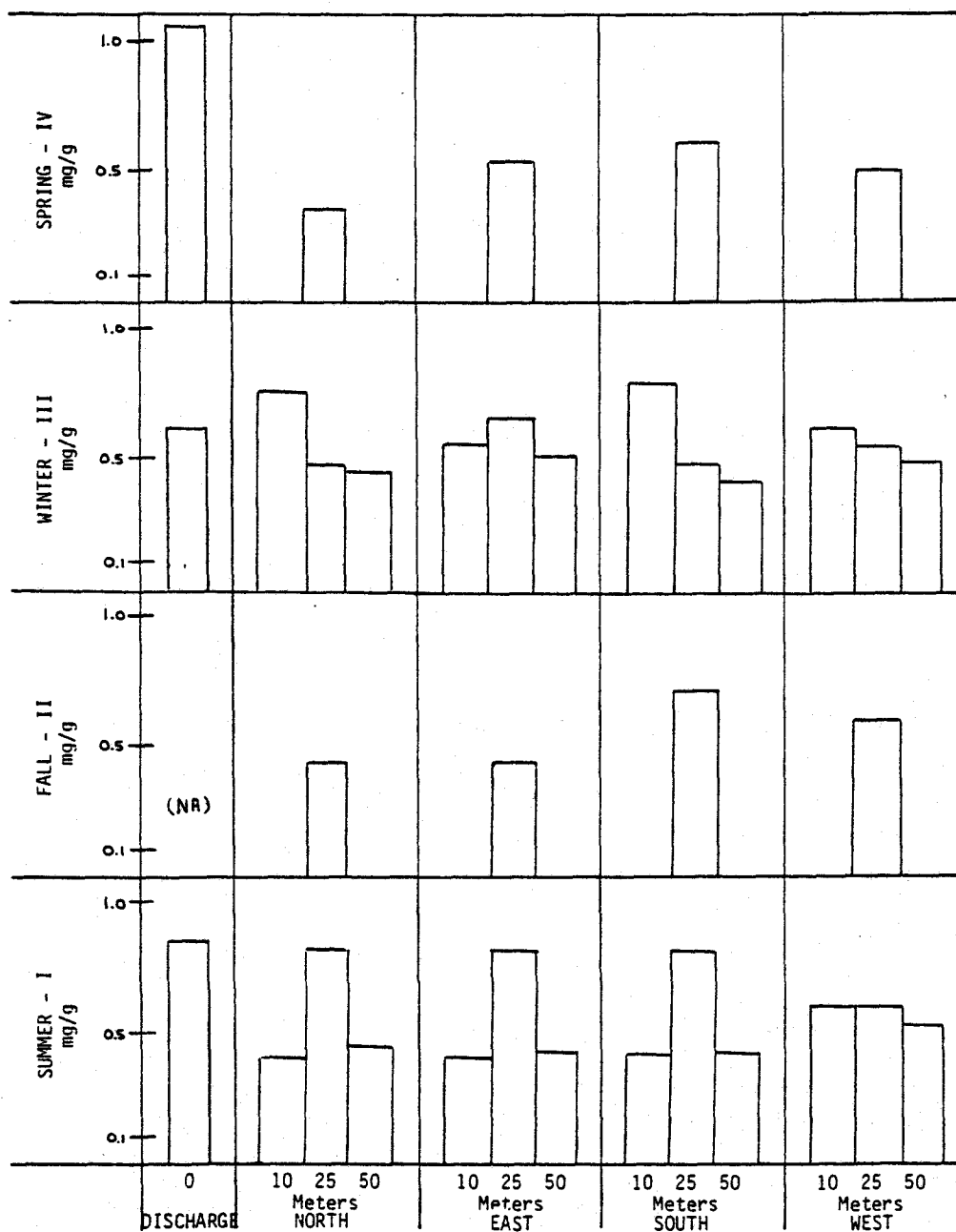


Figure 19. Temporal and Spacial Variation of Fe in Surficial Sediments at Platform 296-B

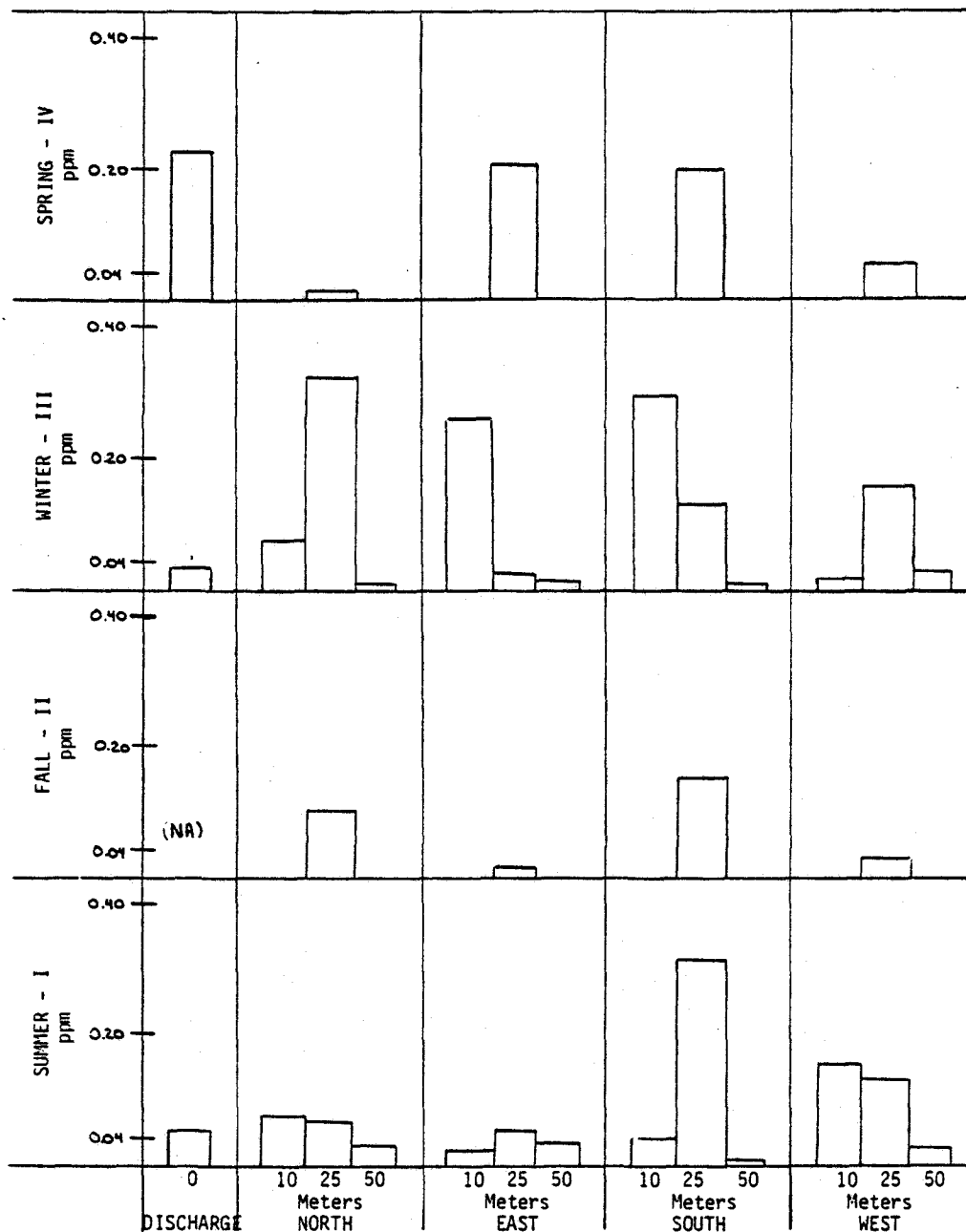


Figure 20. Temporal and Spatial Variation of Hg in Surficial Sediments at Platform 296-B

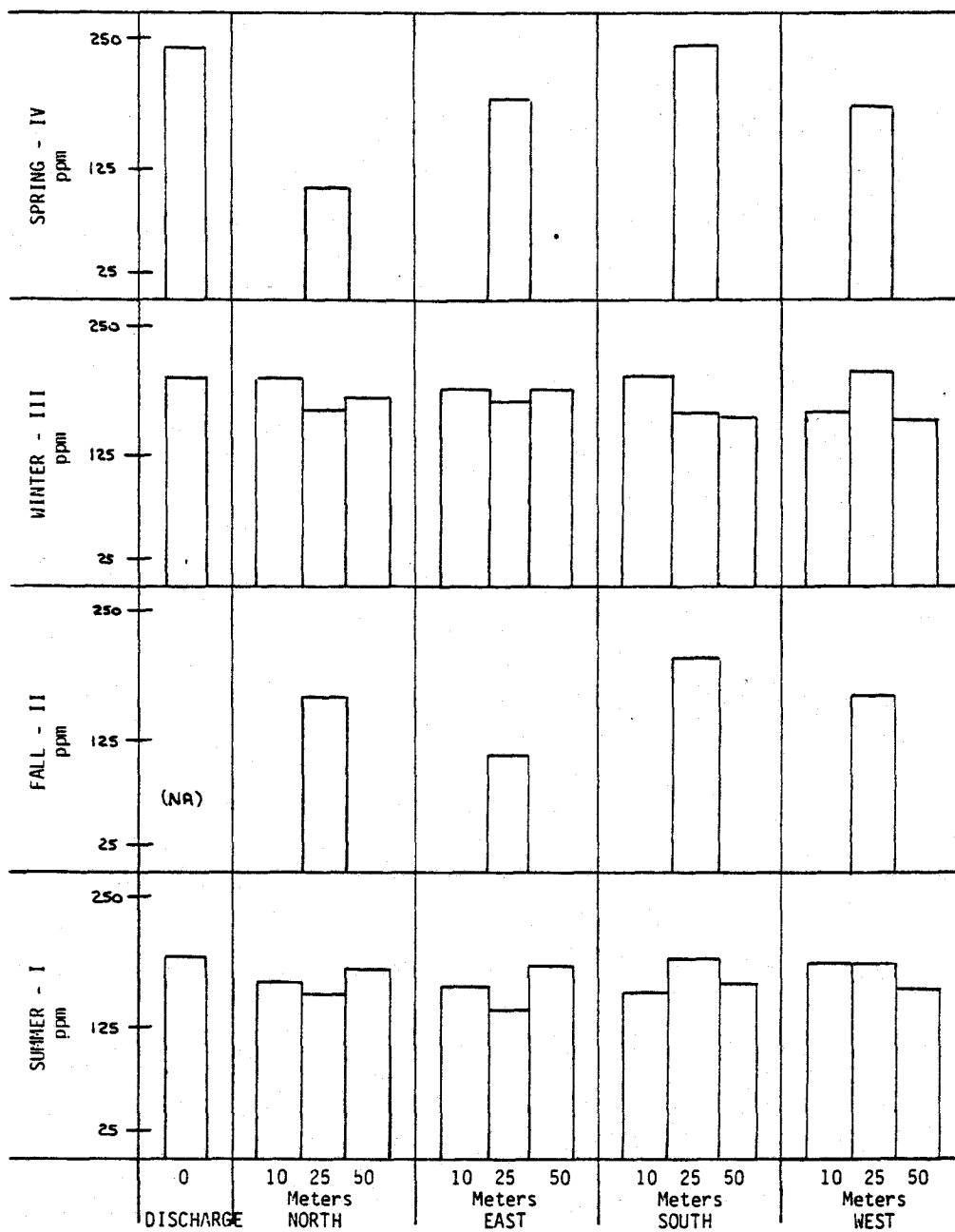


Figure 21. Temporal and Spacial Variation of Mn in Surficial Sediments at Platform 296-B

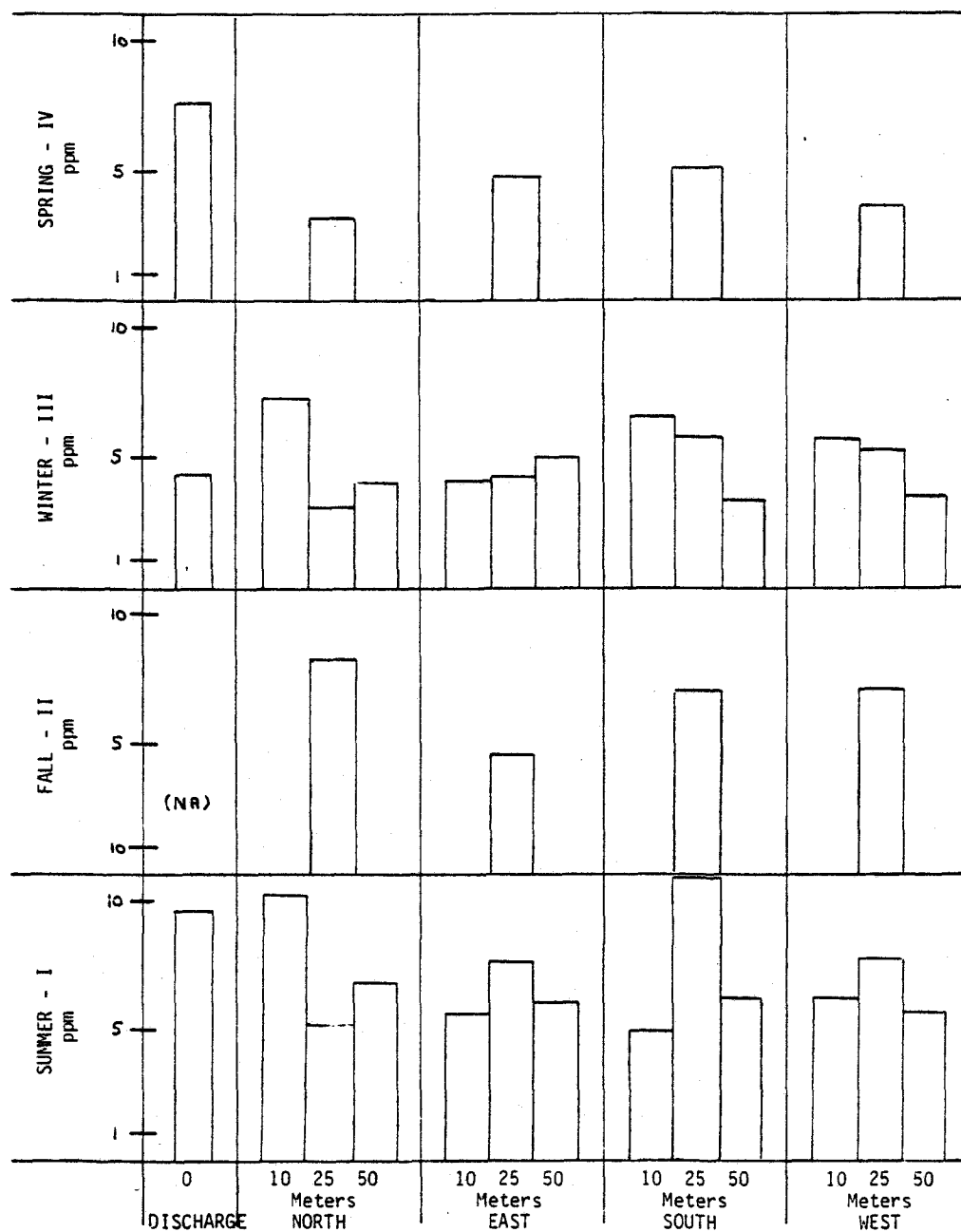


Figure 22. Temporal and Spatial Variation of Ni in Surficial Sediments at Platform 296-B

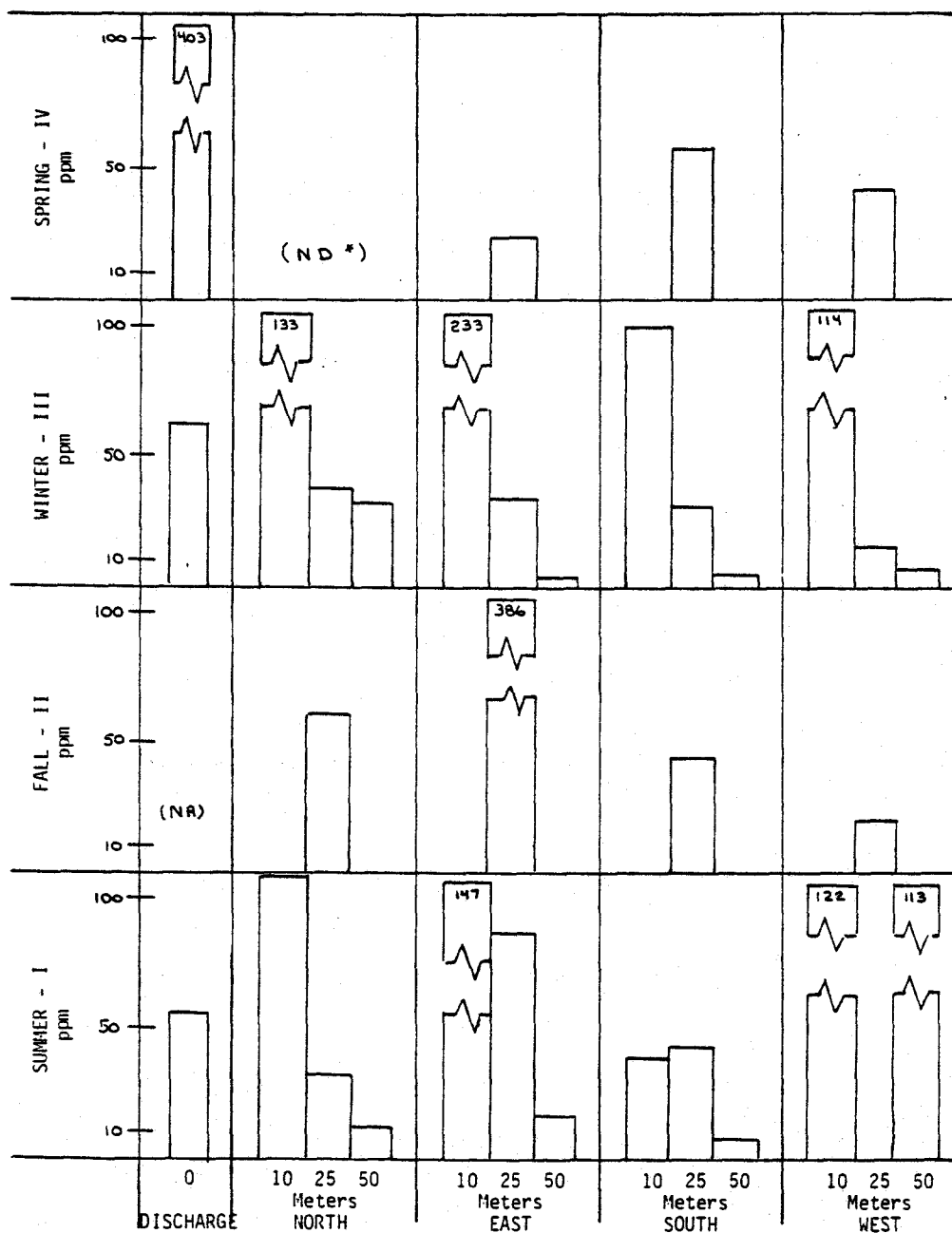


Figure 23. Temporal and Spatial Variation of Pb in Surficial Sediments at Platform 296-B

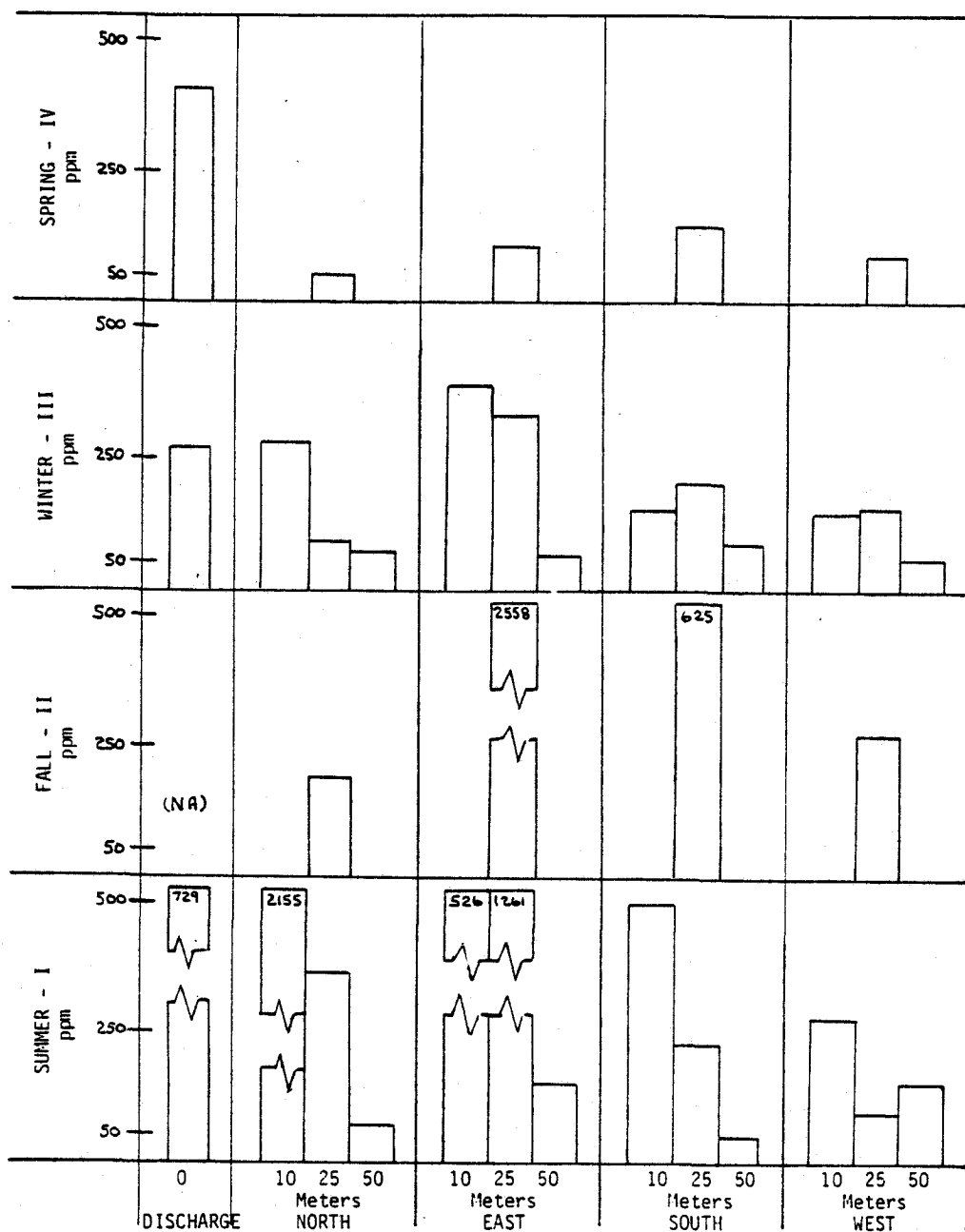


Figure 24. Temporal and Spatial Variation of Sr in Surficial Sediments at Platform 296-B

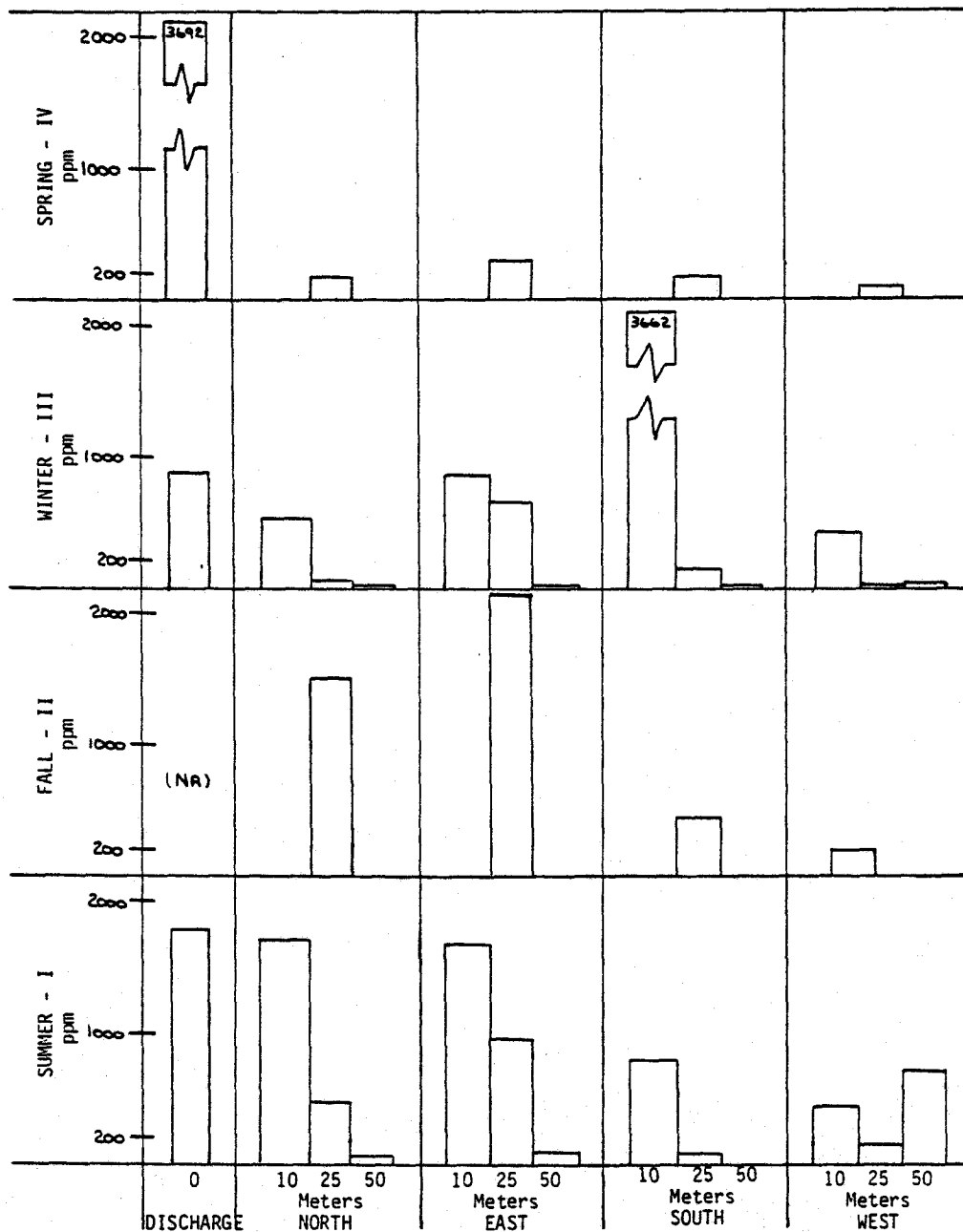


Figure 25. Temporal and Spatial Variation of Zn in Surficial Sediments at Platform 296-B

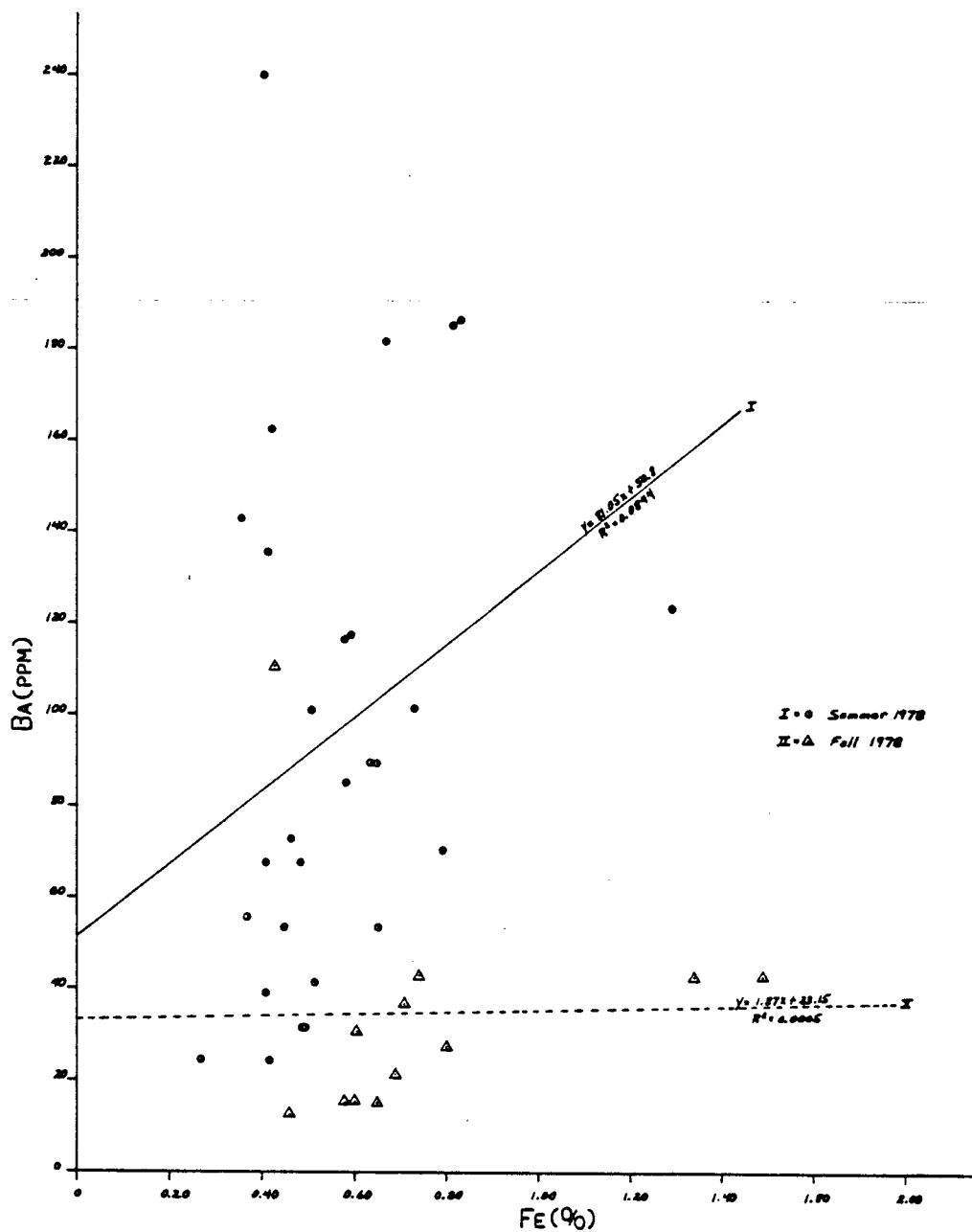


Figure 26. Scatter Plot of Ba versus Fe Concentration in Surficial Sediments During Cruise I and II

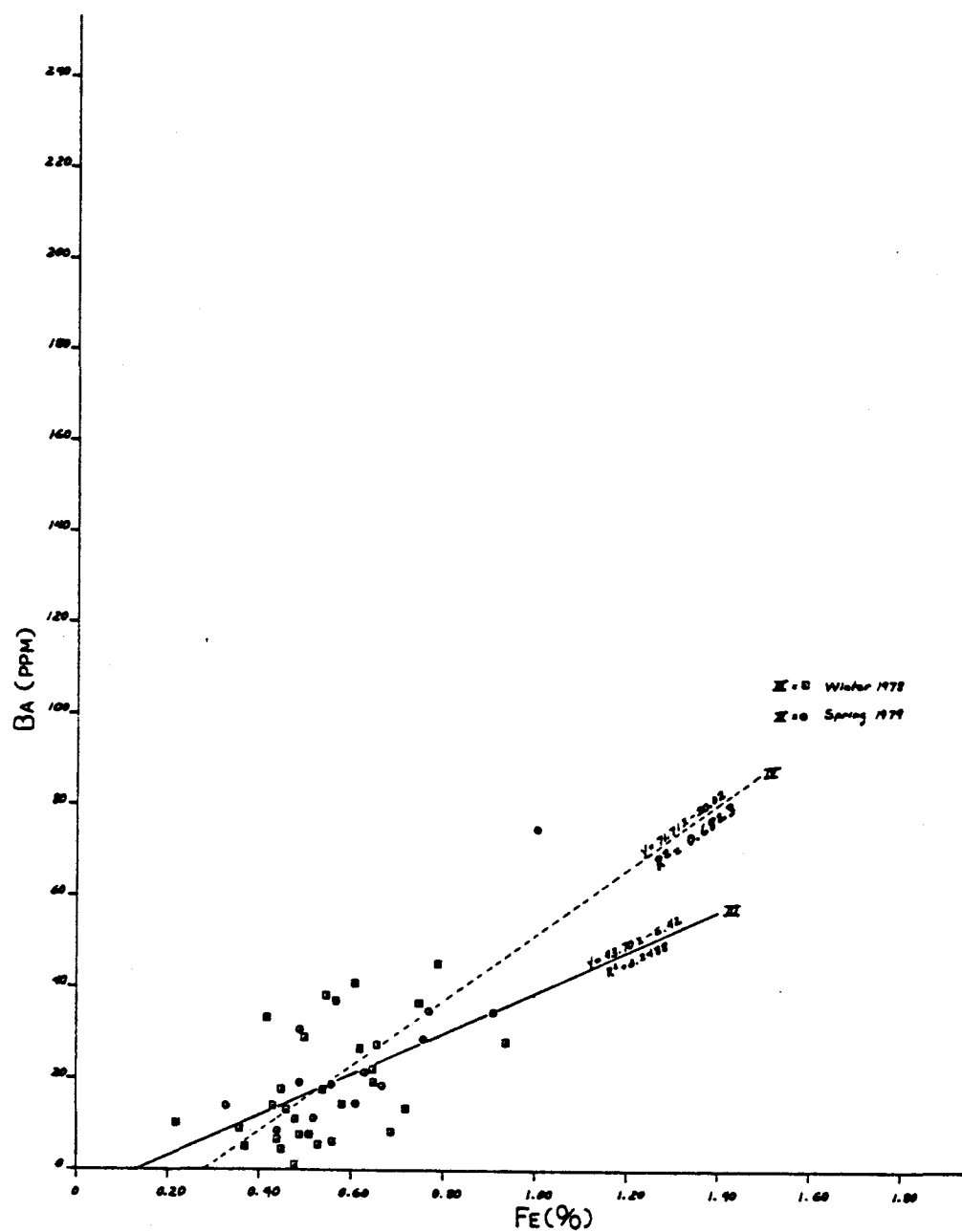


Figure 27. Scatter Plot of Ba versus Fe Concentration in Surficial Sediments During Cruise III and IV

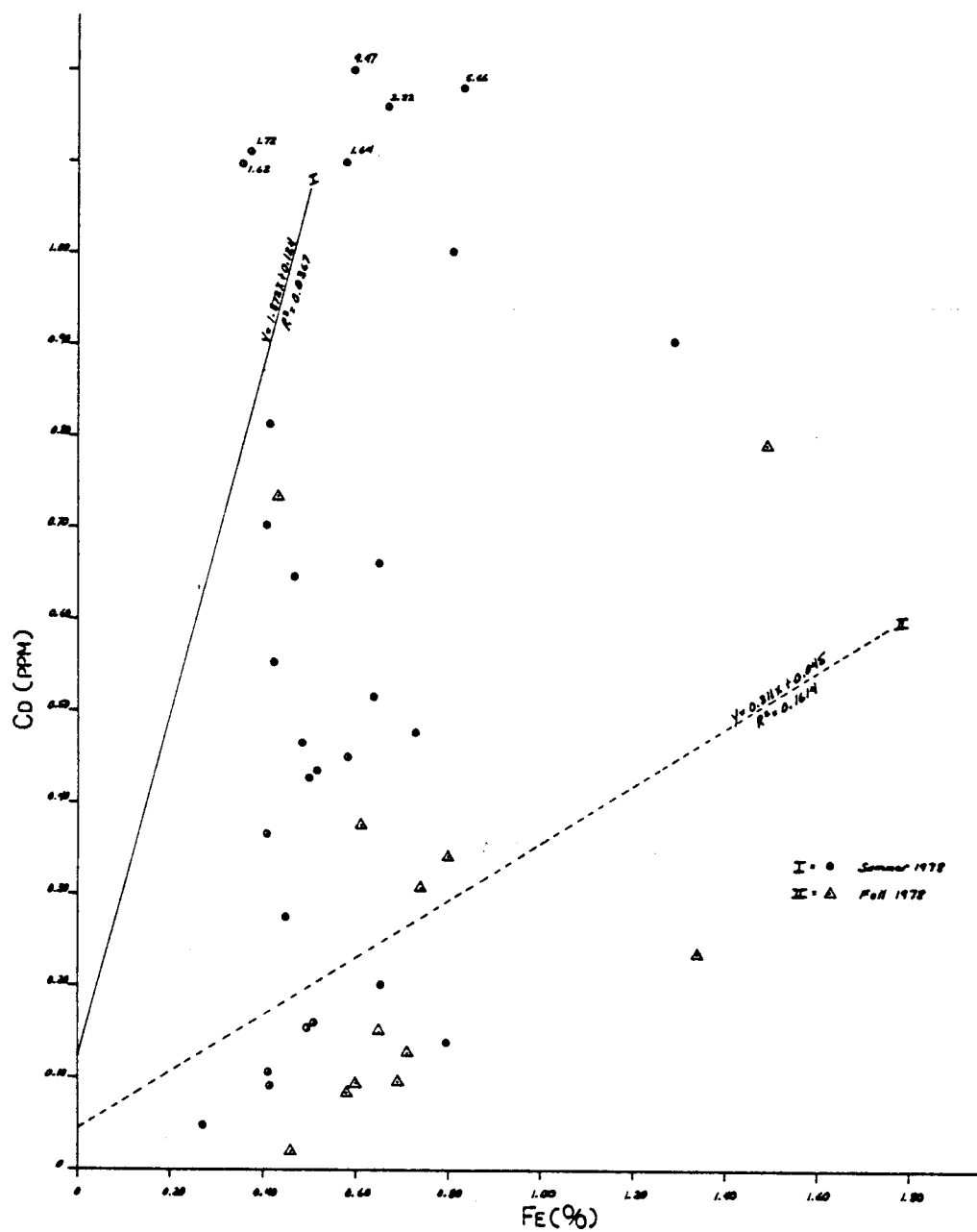


Figure 28. Scatter Plot of Cd versus Fe Concentration in Surficial Sediments During Cruise I and II

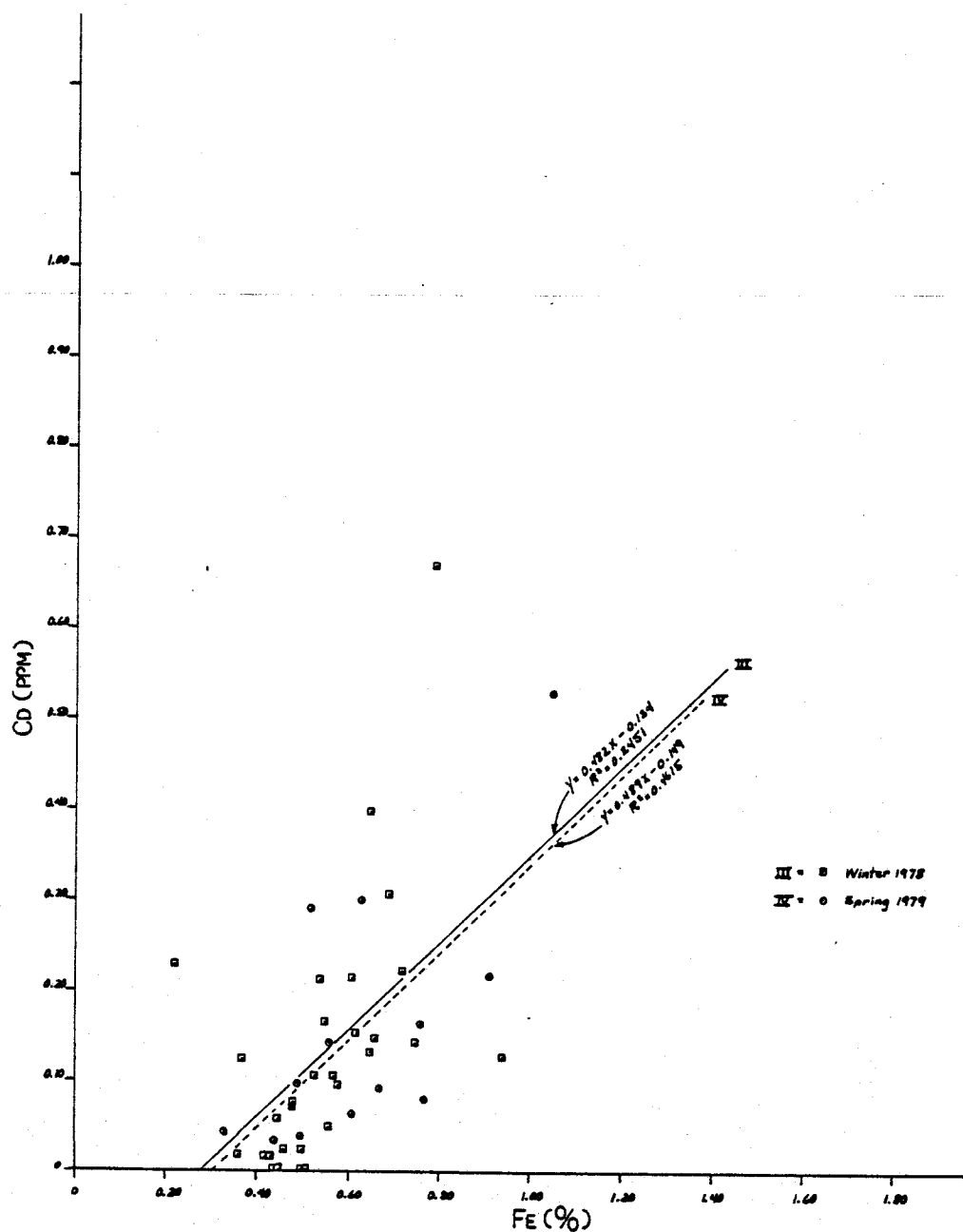


Figure 29. Scatter Plot of Cd versus Fe Concentration in Surficial Sediments During Cruise III and IV

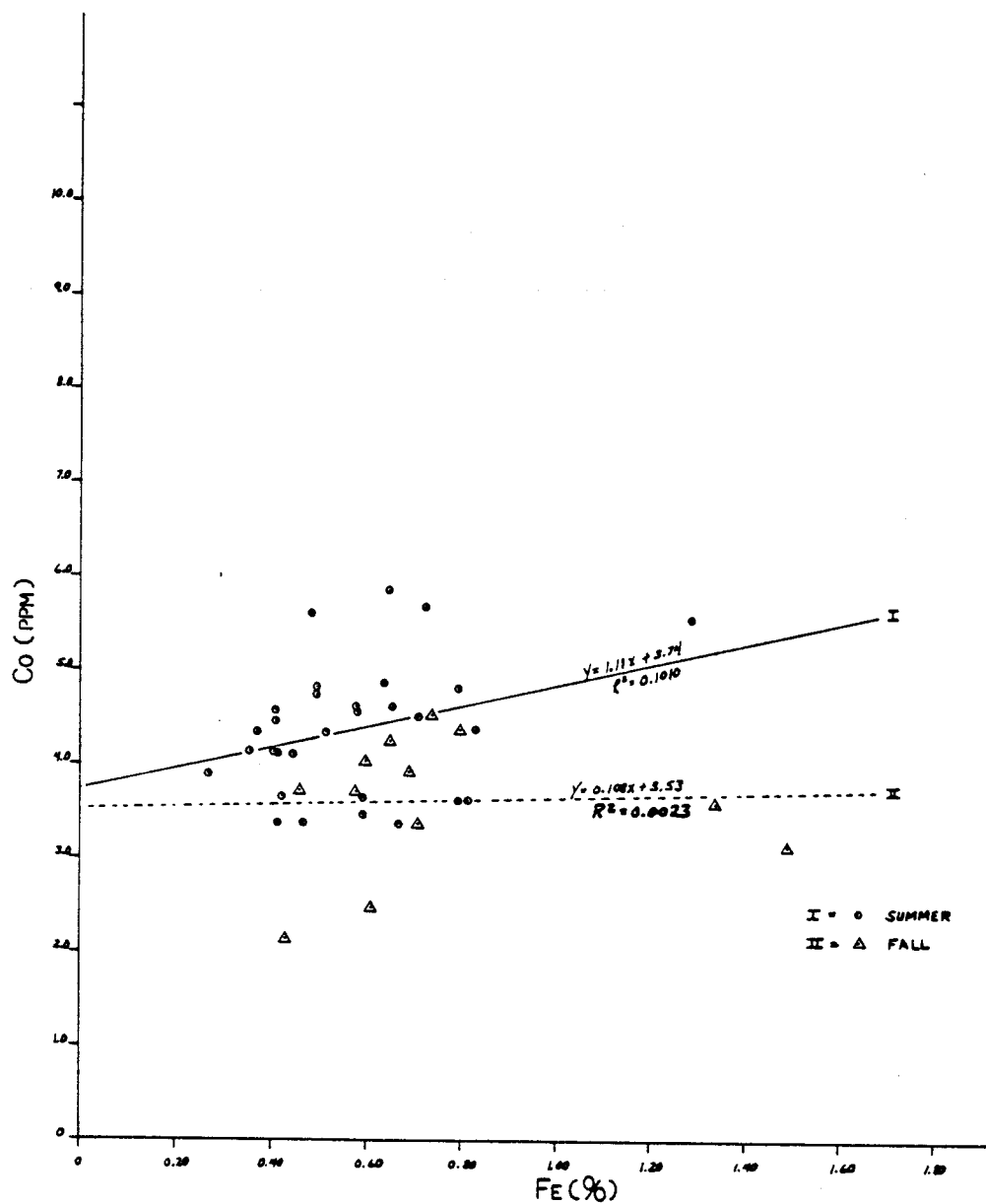


Figure 30. Scatter Plot of Co versus Fe Concentration in Surficial Sediments During Cruise I and II

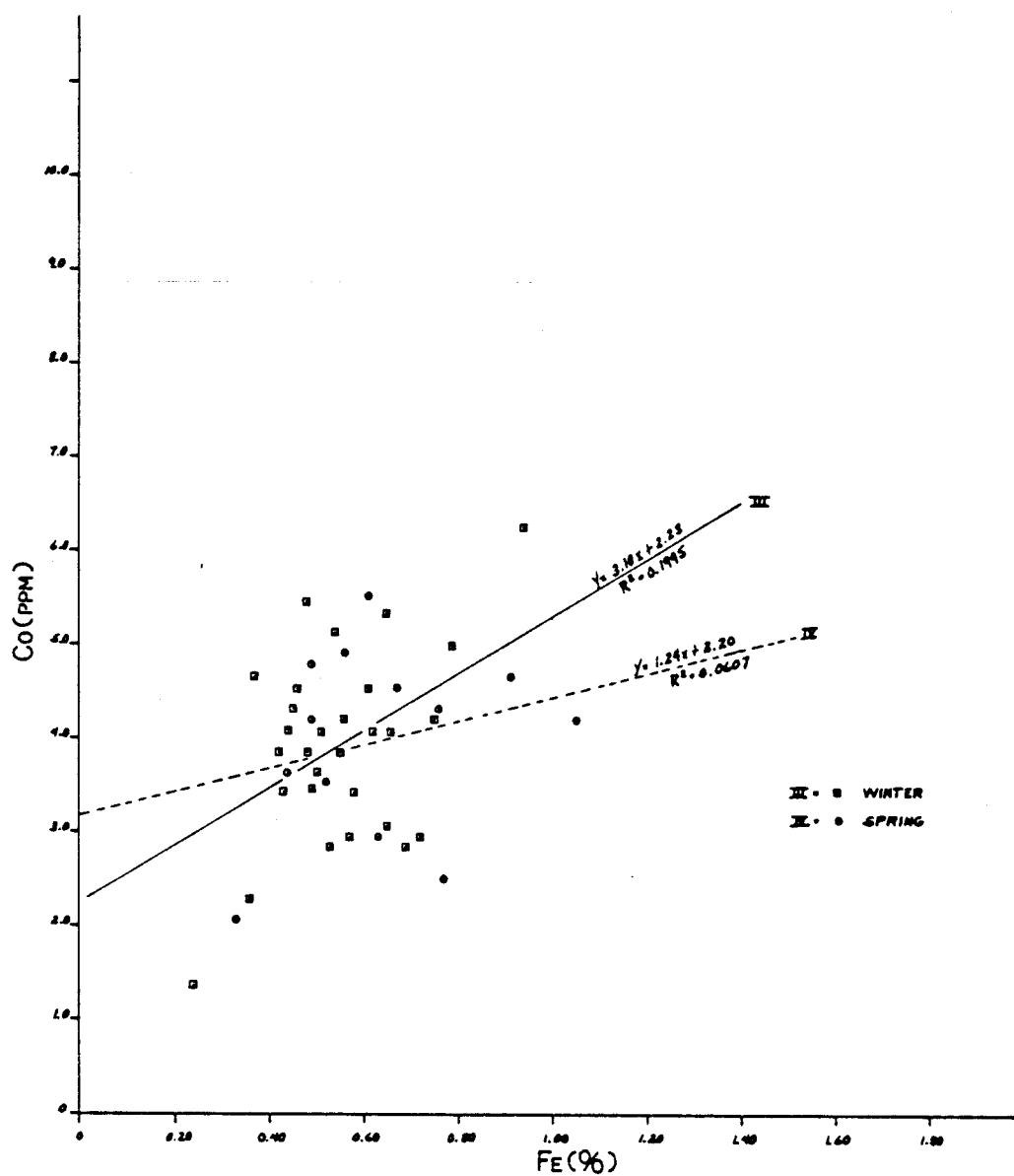


Figure 31. Scatter Plot of Co versus Fe Concentration in Surficial Sediments During Cruise III and IV

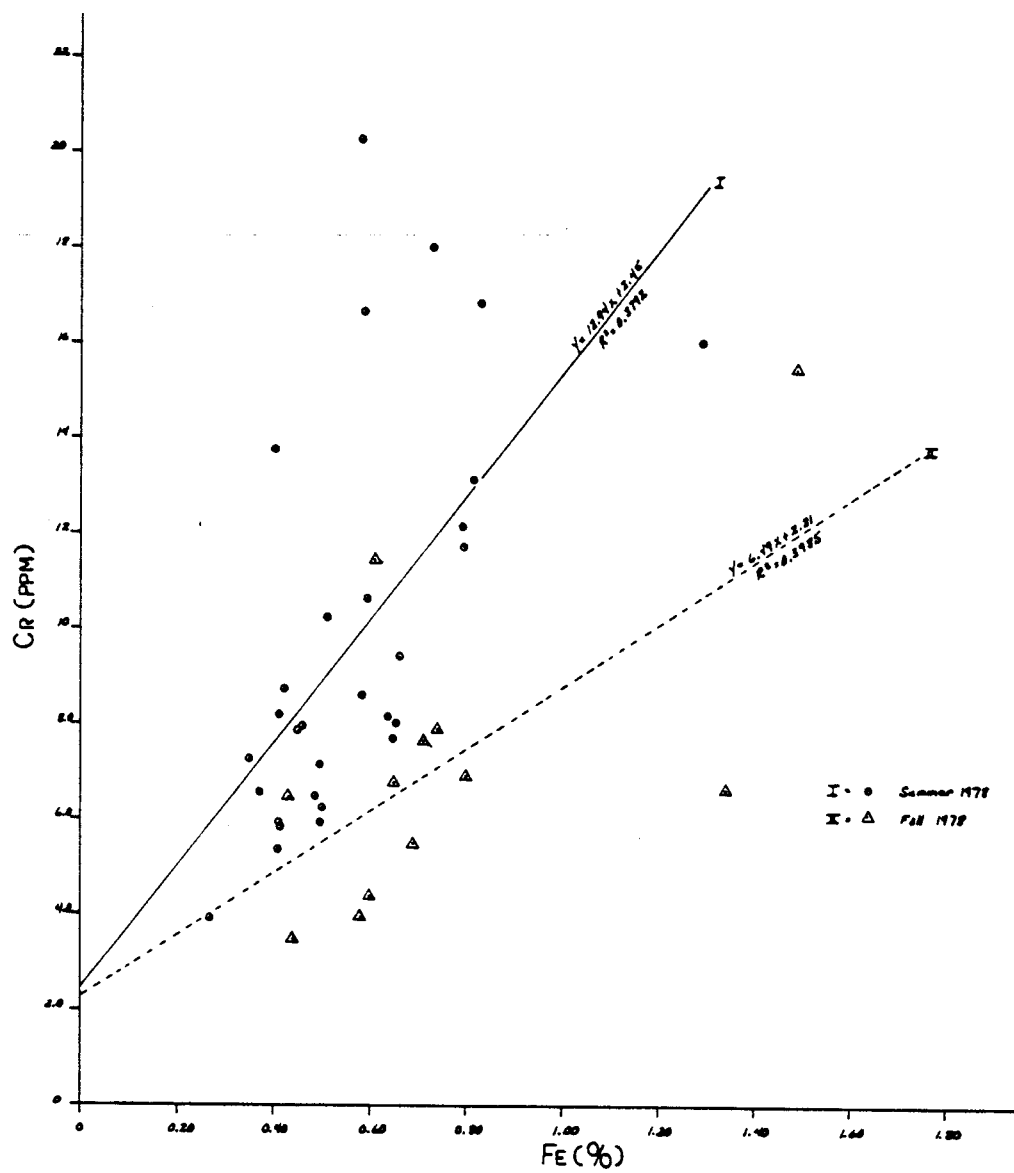


Figure 32. Scatter Plot of Cr versus Fe Concentration in Surficial Sediments During Cruise I and II

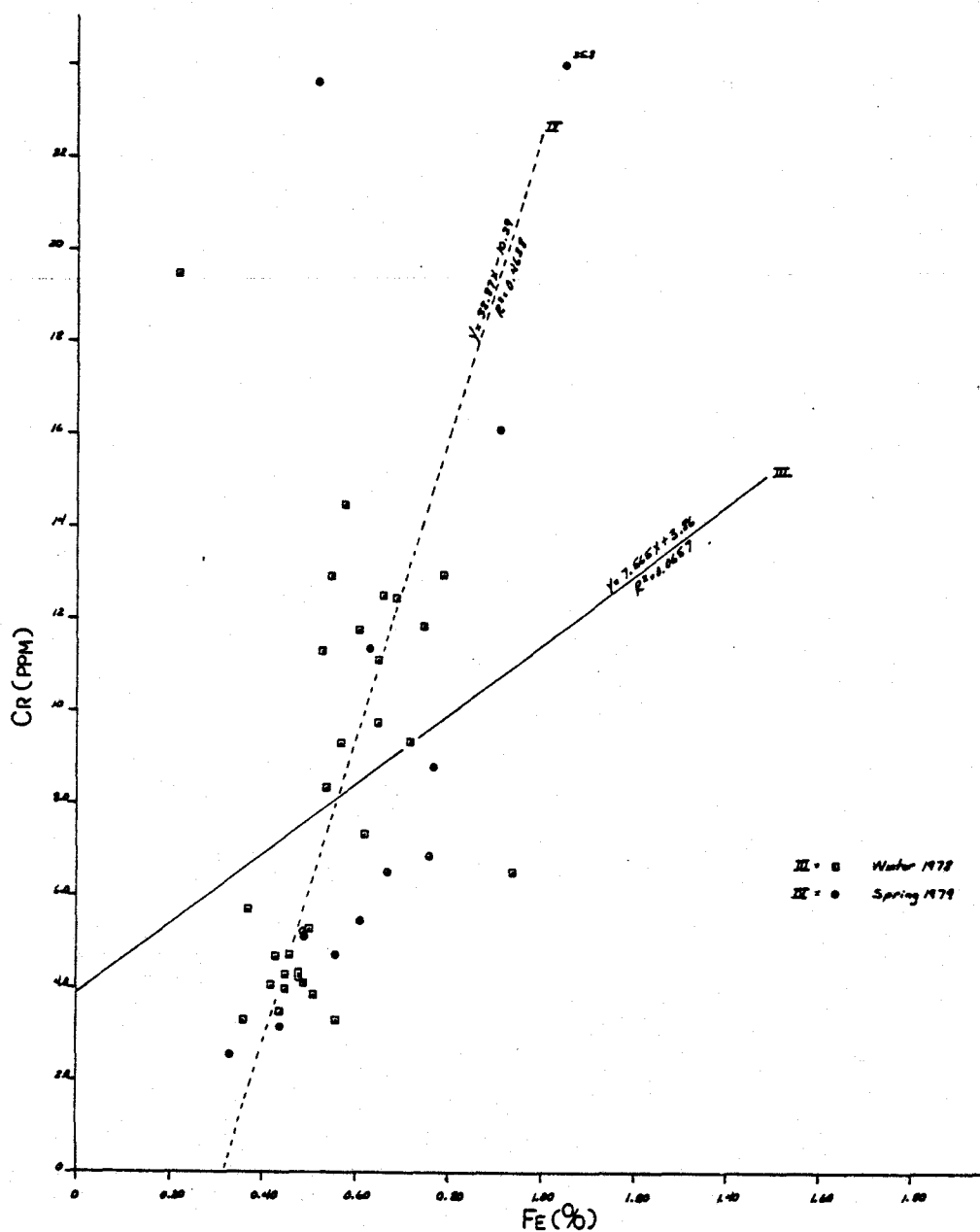


Figure 33. Scatter Plot of Cr versus Fe Concentration in Surficial Sediments During Cruise III and IV

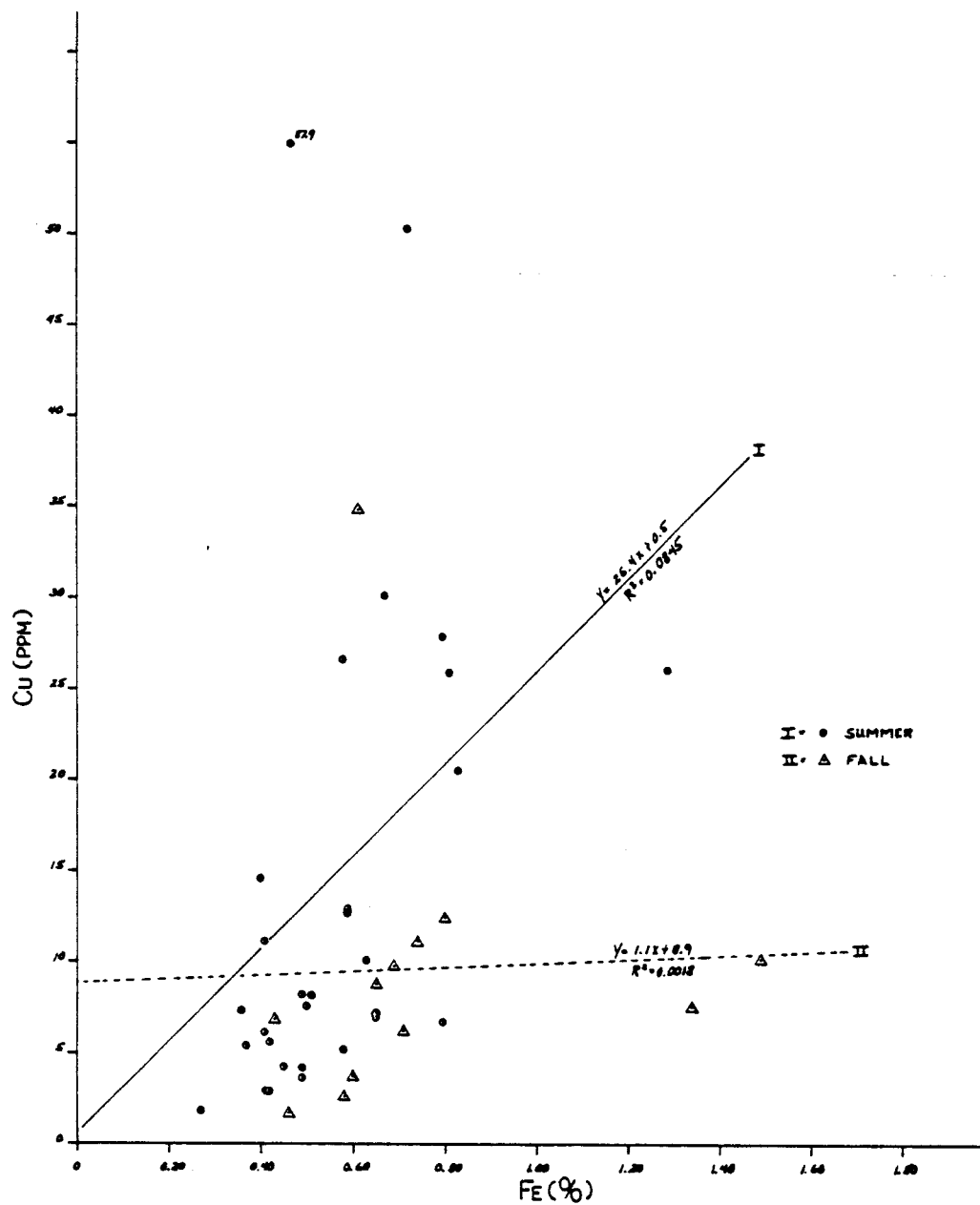


Figure 34. Scatter Plot of Cu. versus Fe Concentration in Surficial Sediments During Cruise I and II

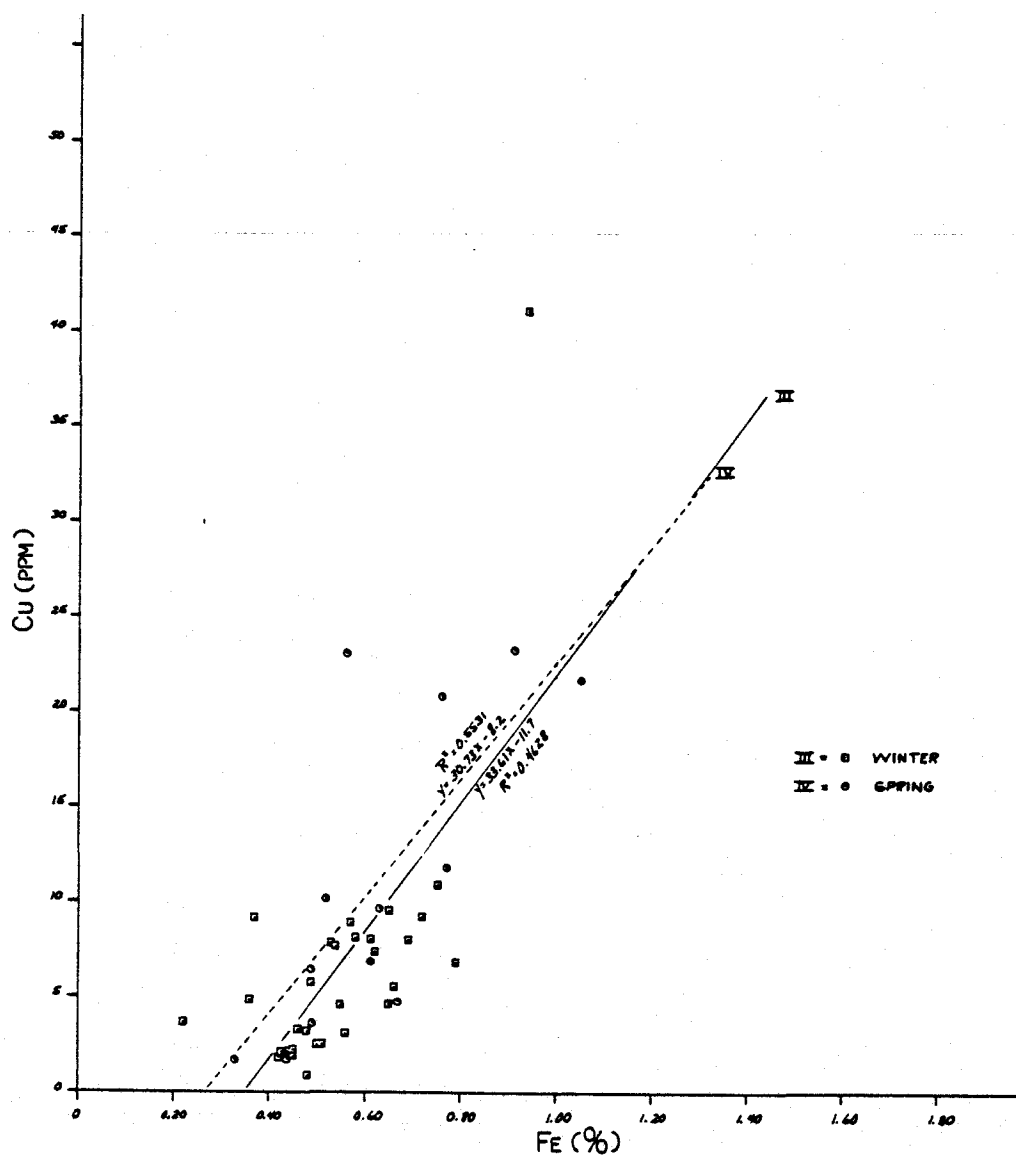


Figure 35. Scatter Plot of Cu versus Fe Concentration in Surficial Sediments During Cruise III and IV

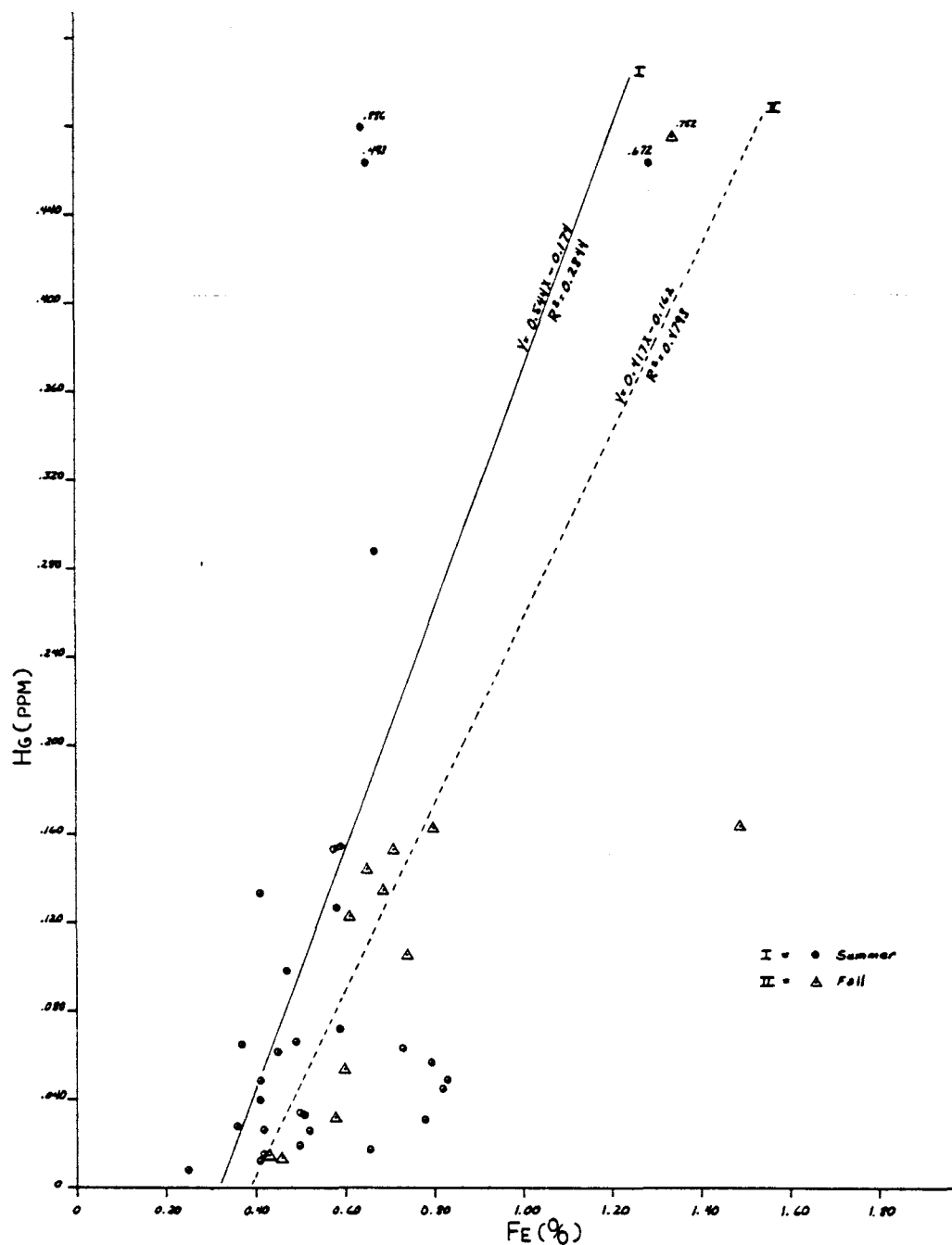


Figure 36. Scatter Plot of Hg versus Fe Concentration in Surficial Sediments During Cruise I and II

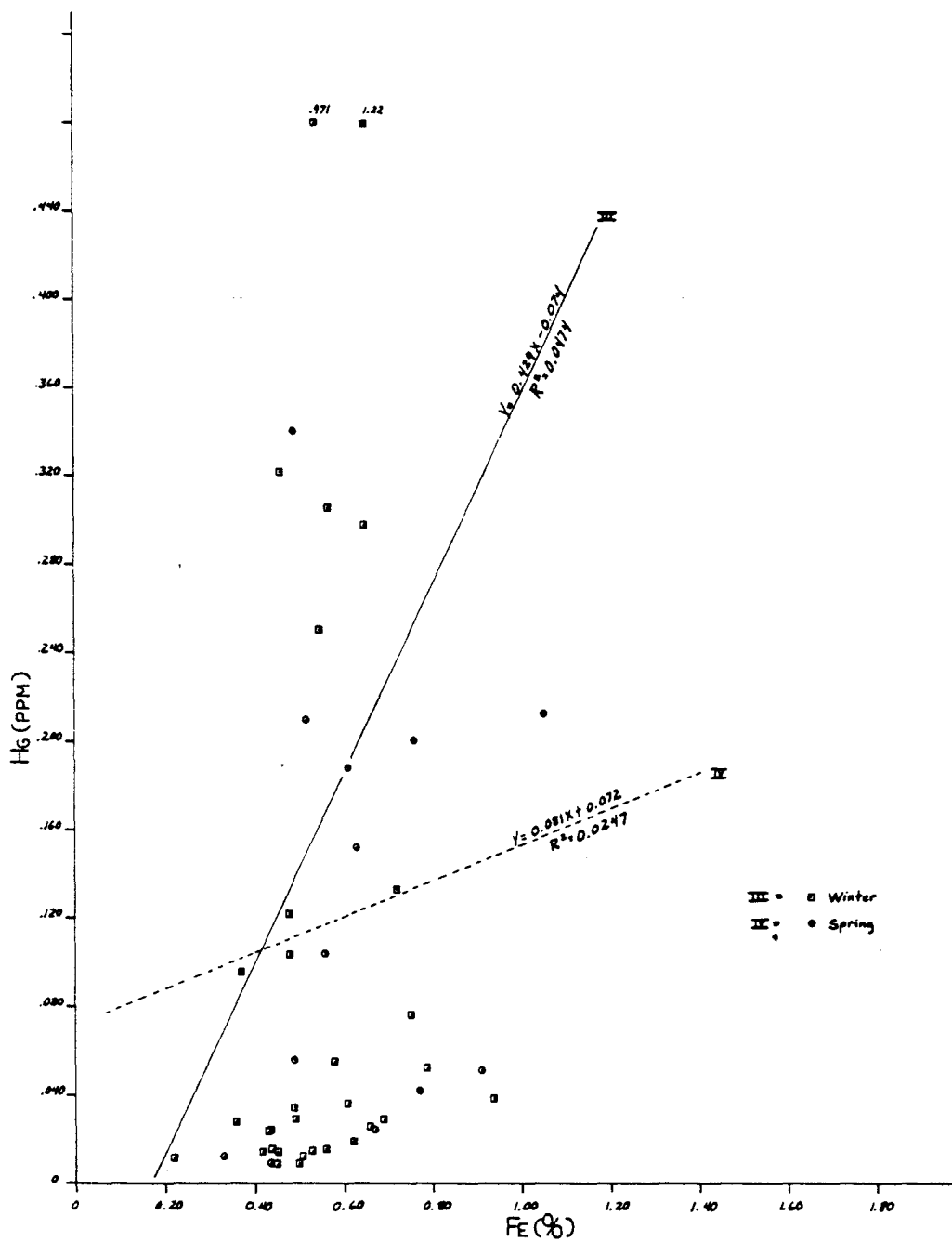


Figure 37. Scatter Plot of Hg versus Fe Concentration in Surficial Sediments During Cruise III and IV

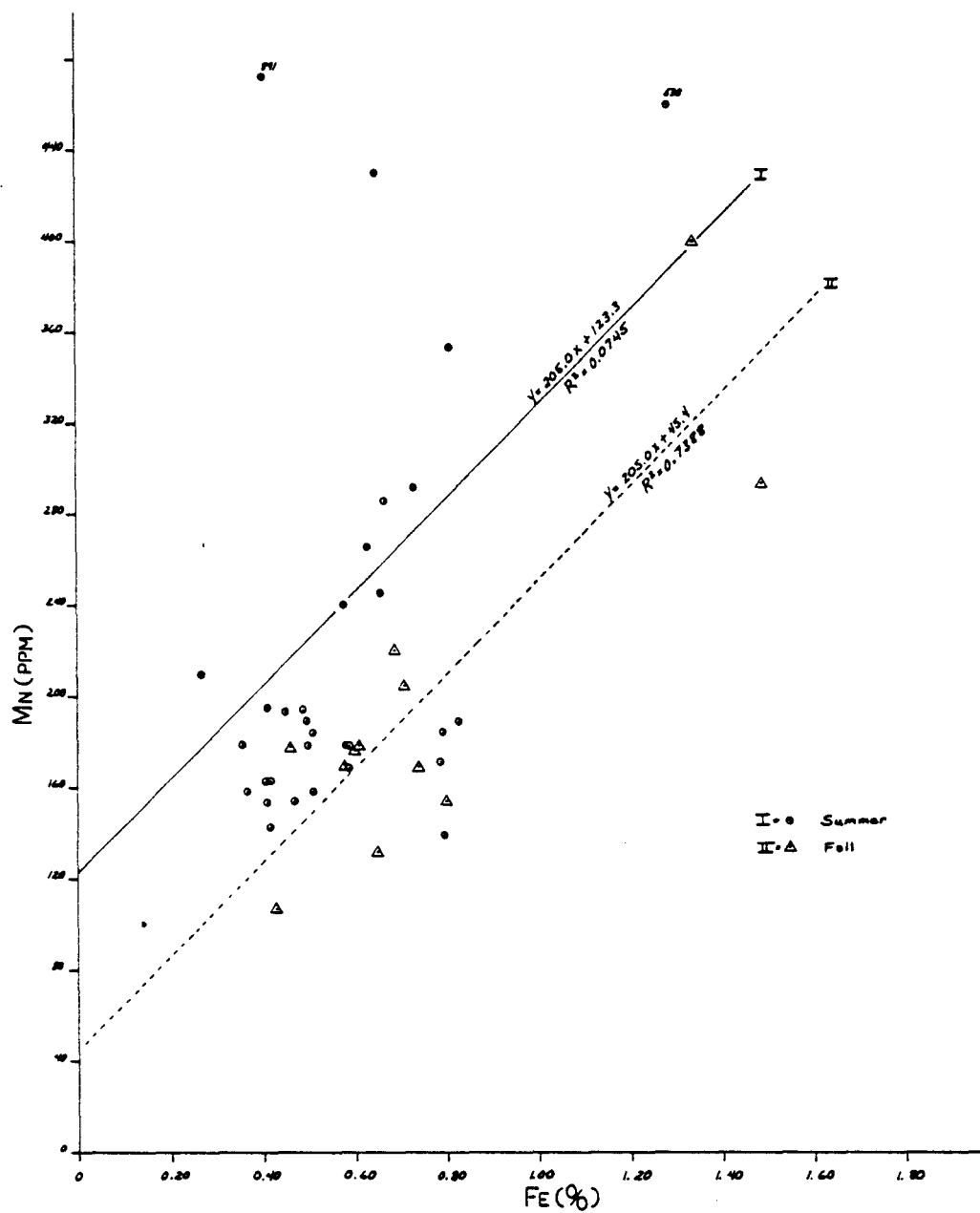


Figure 38. Scatter Plot of Mn versus Fe Concentration in Surficial Sediments During Cruise I and II

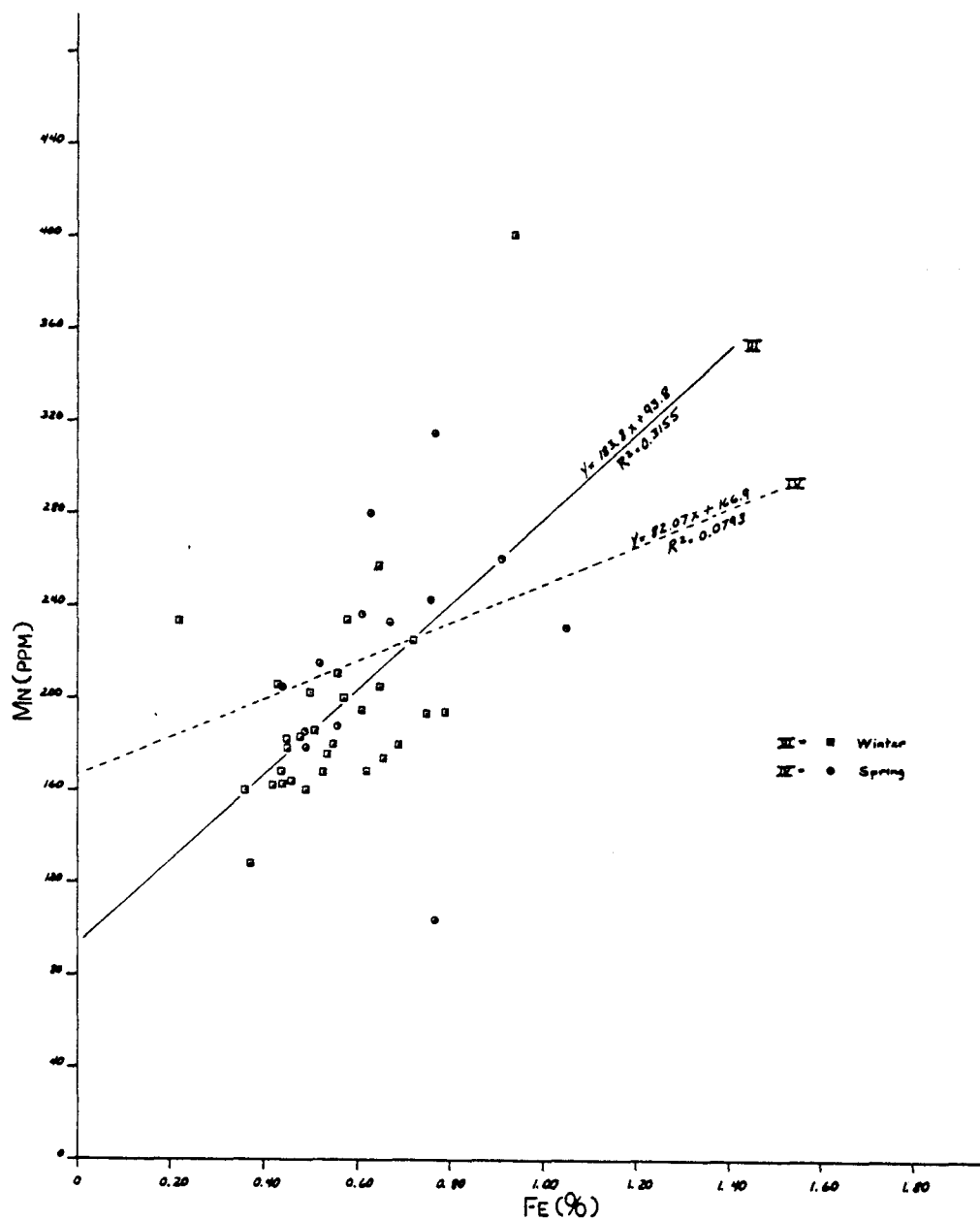


Figure 39. Scatter Plot of Mn versus Fe Concentration in Surficial Sediments During Cruise III and IV

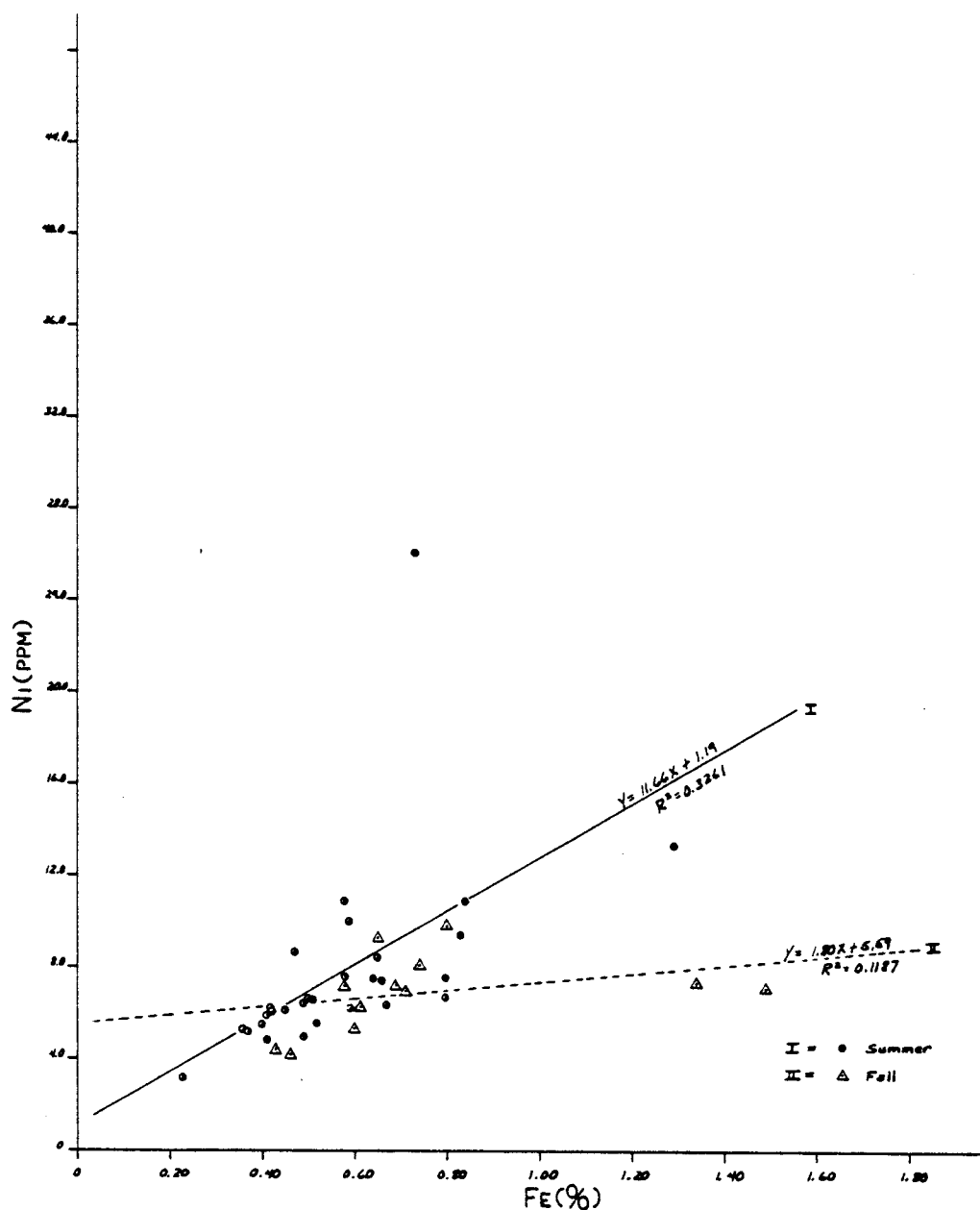


Figure 40. Scatter Plot of Ni versus Fe Concentration in Surficial Sediments During Cruise I and II

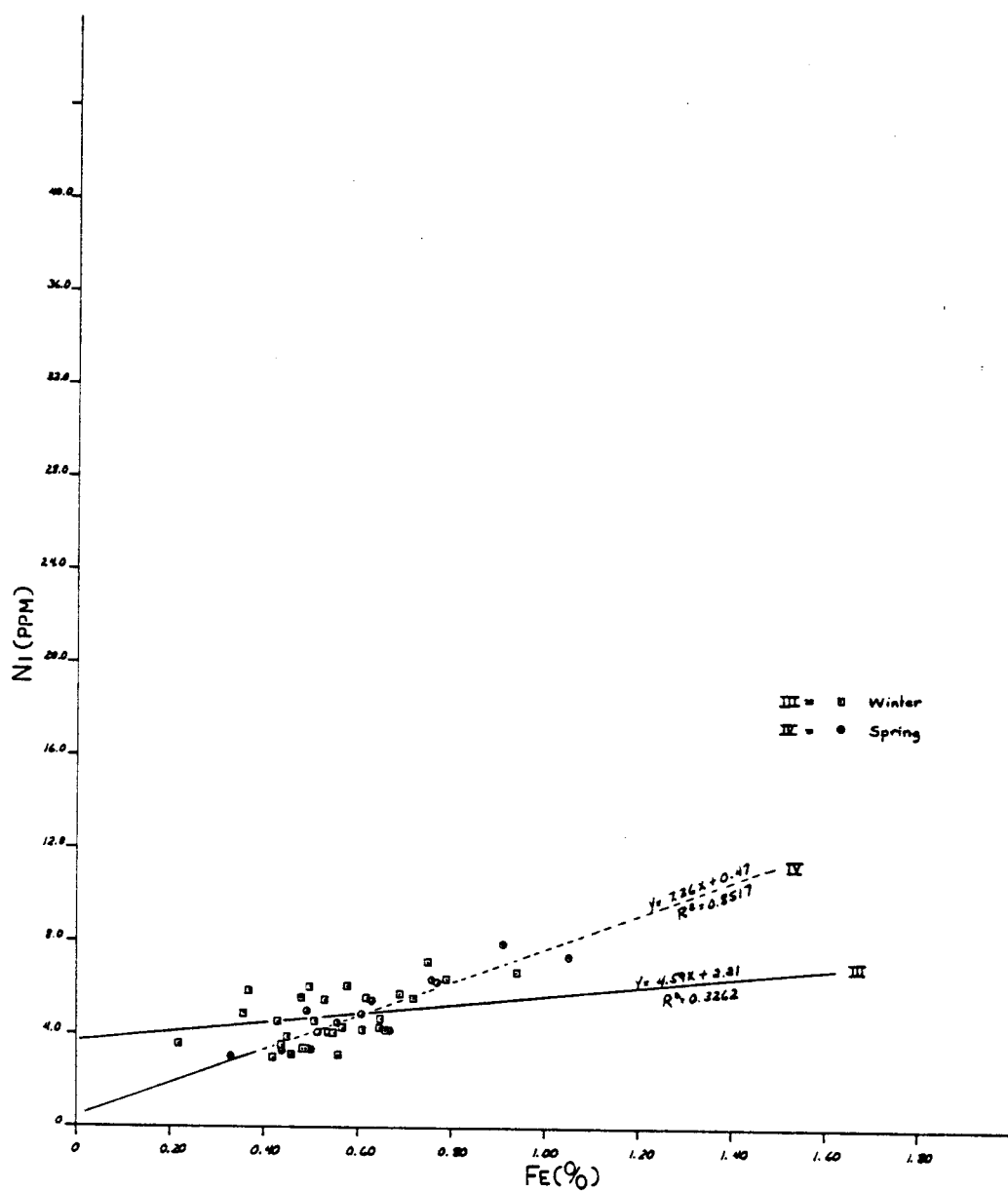


Figure 41. Scatter Plot of Ni versus Fe Concentration in Surficial Sediments During Cruise III and IV

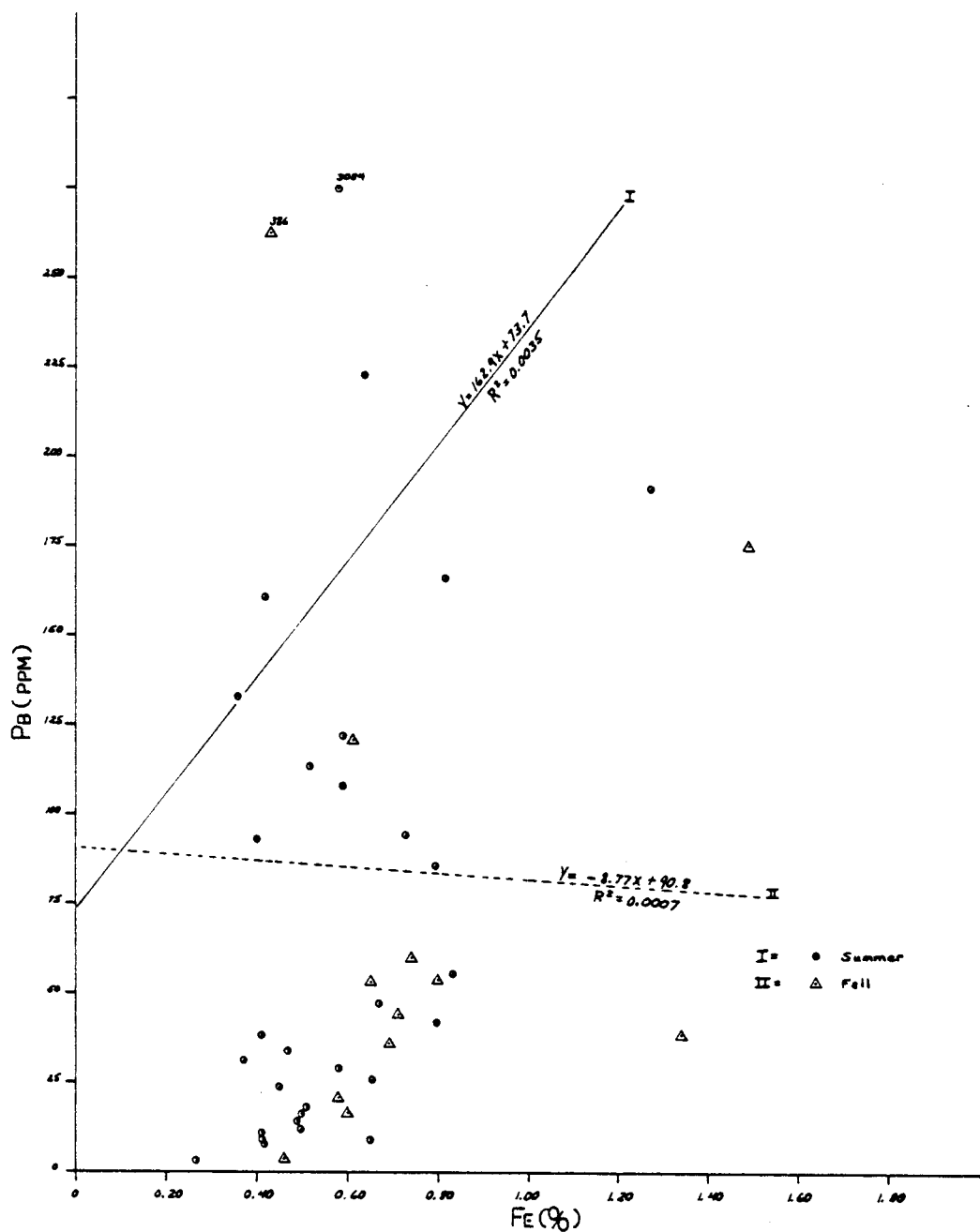


Figure 42. Scatter Plot of Pb versus Fe Concentration in Surficial Sediments During Cruise I and II

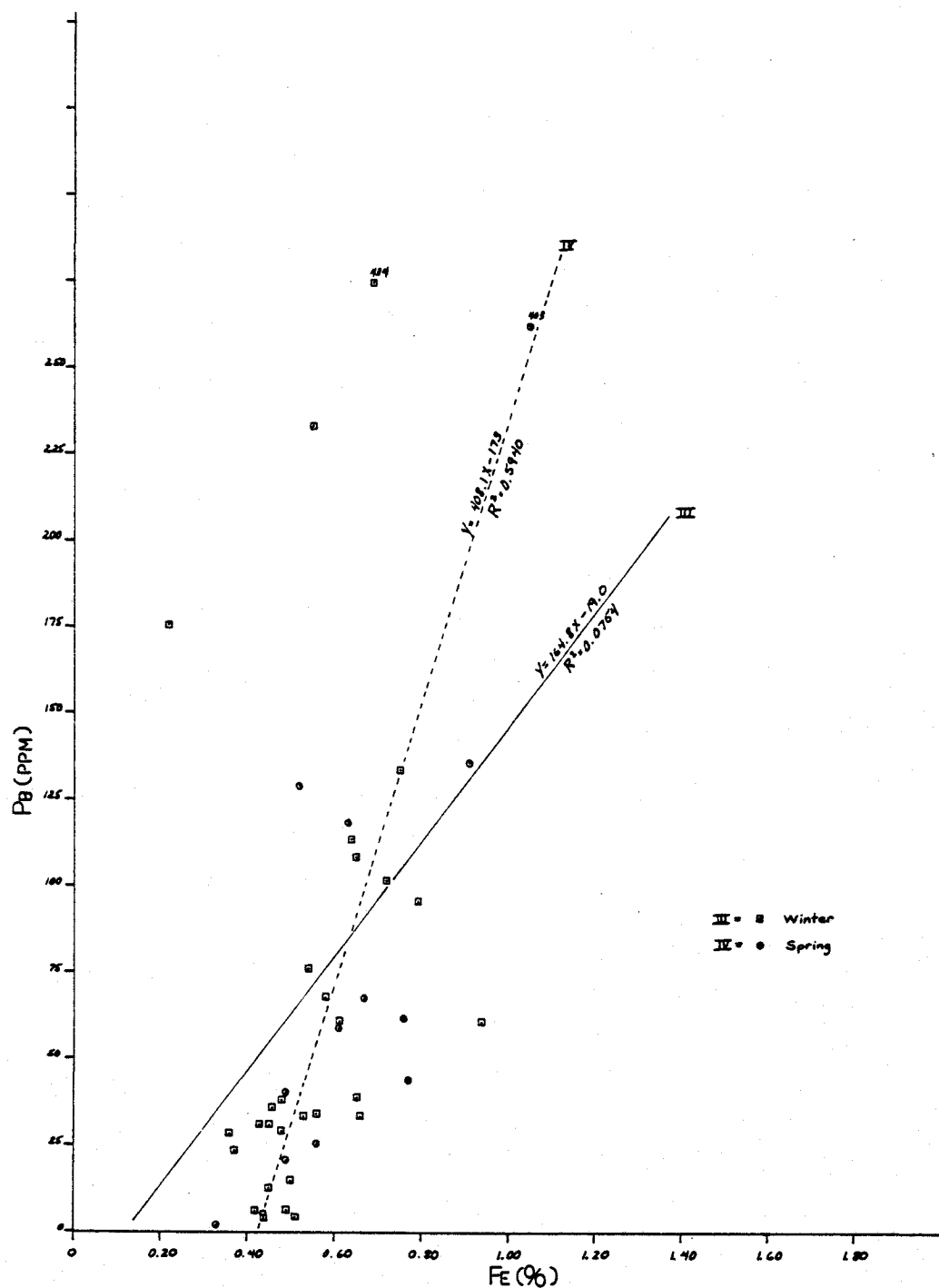


Figure 43. Scatter Plot of Pb versus Fe Concentration in Surficial Sediments During Cruise III and IV

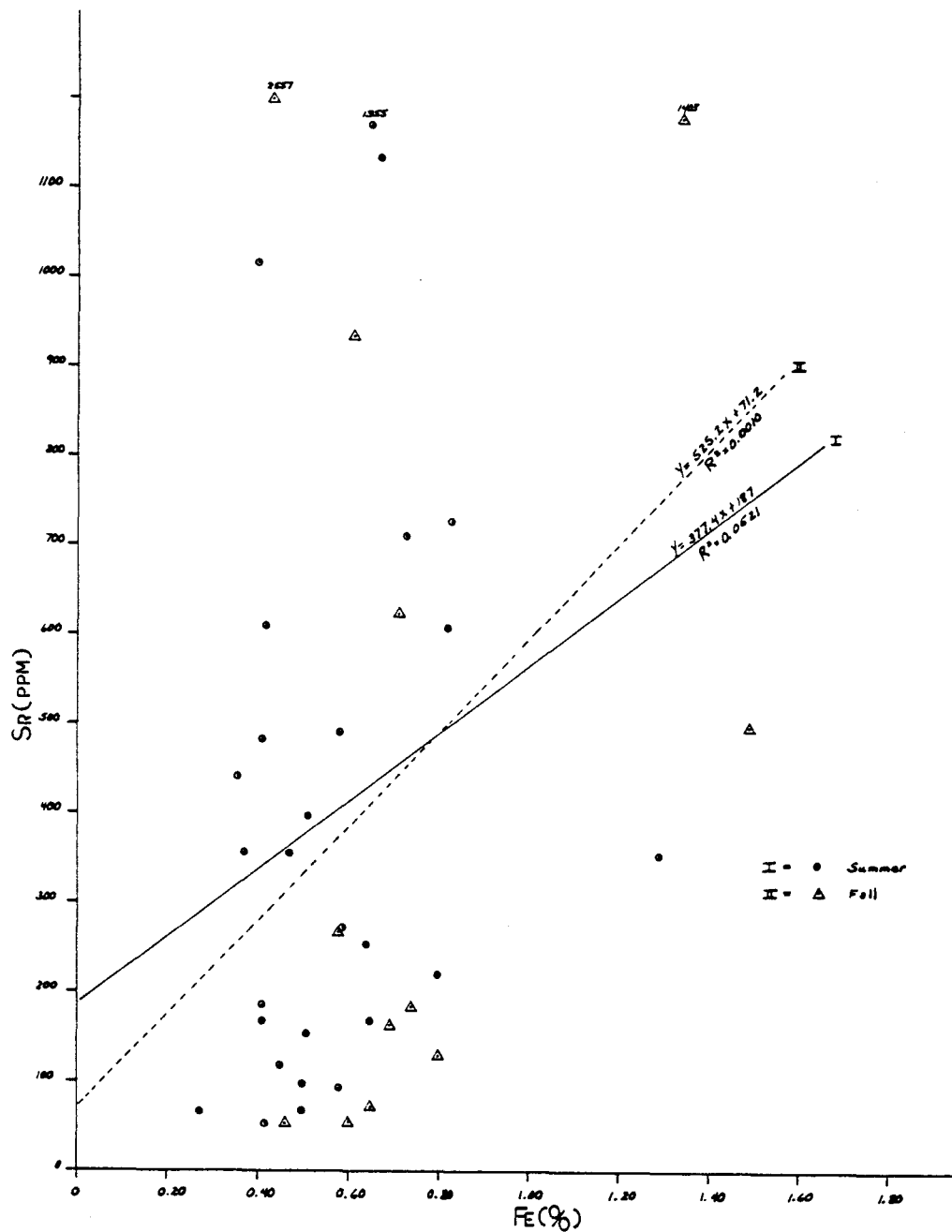


Figure 44. Scatter Plot of Sr versus Fe Concentration in Surficial Sediments During Cruise I and II

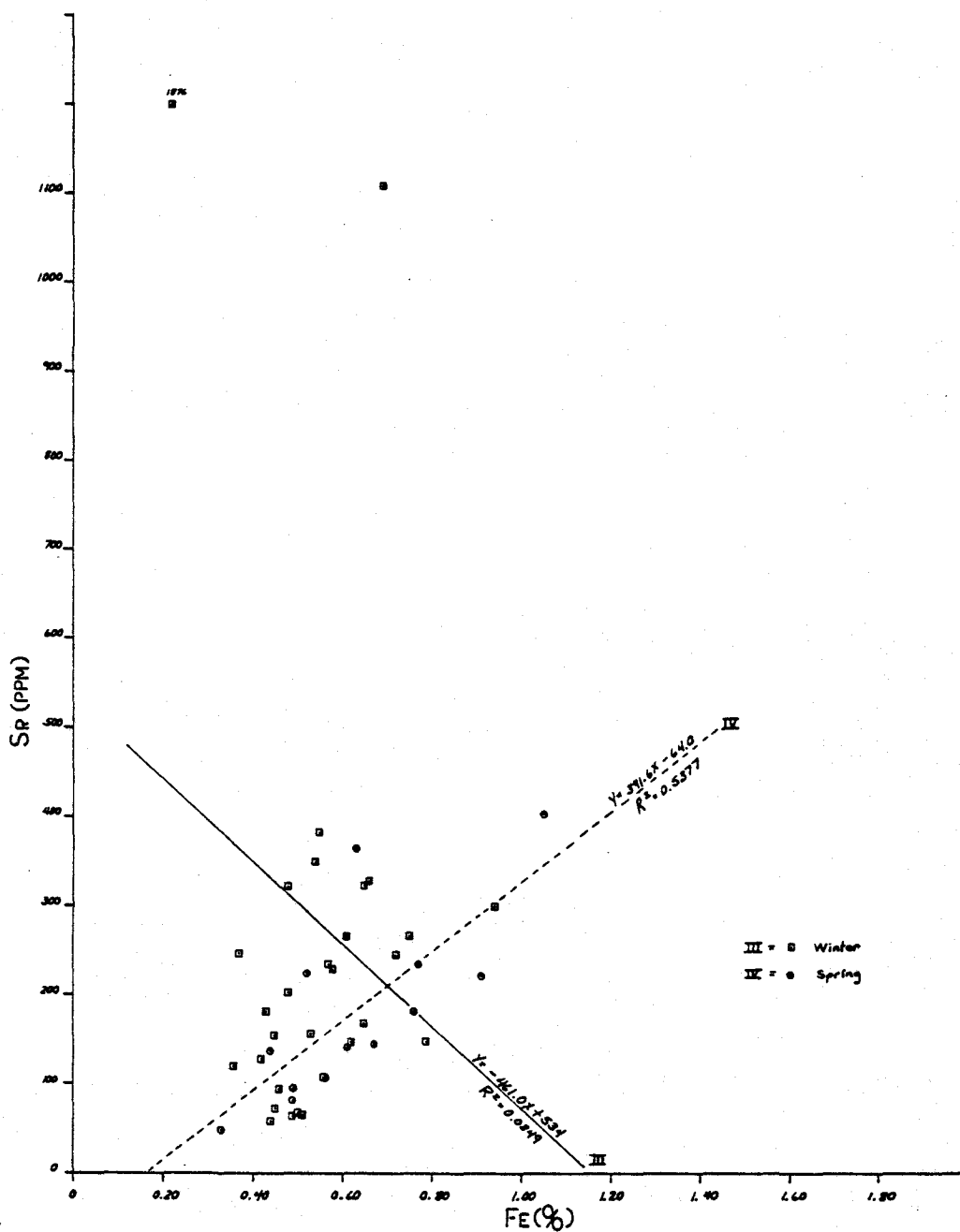


Figure 45. Scatter Plot of Sr versus Fe Concentration in Surficial Sediments During Cruise III and IV

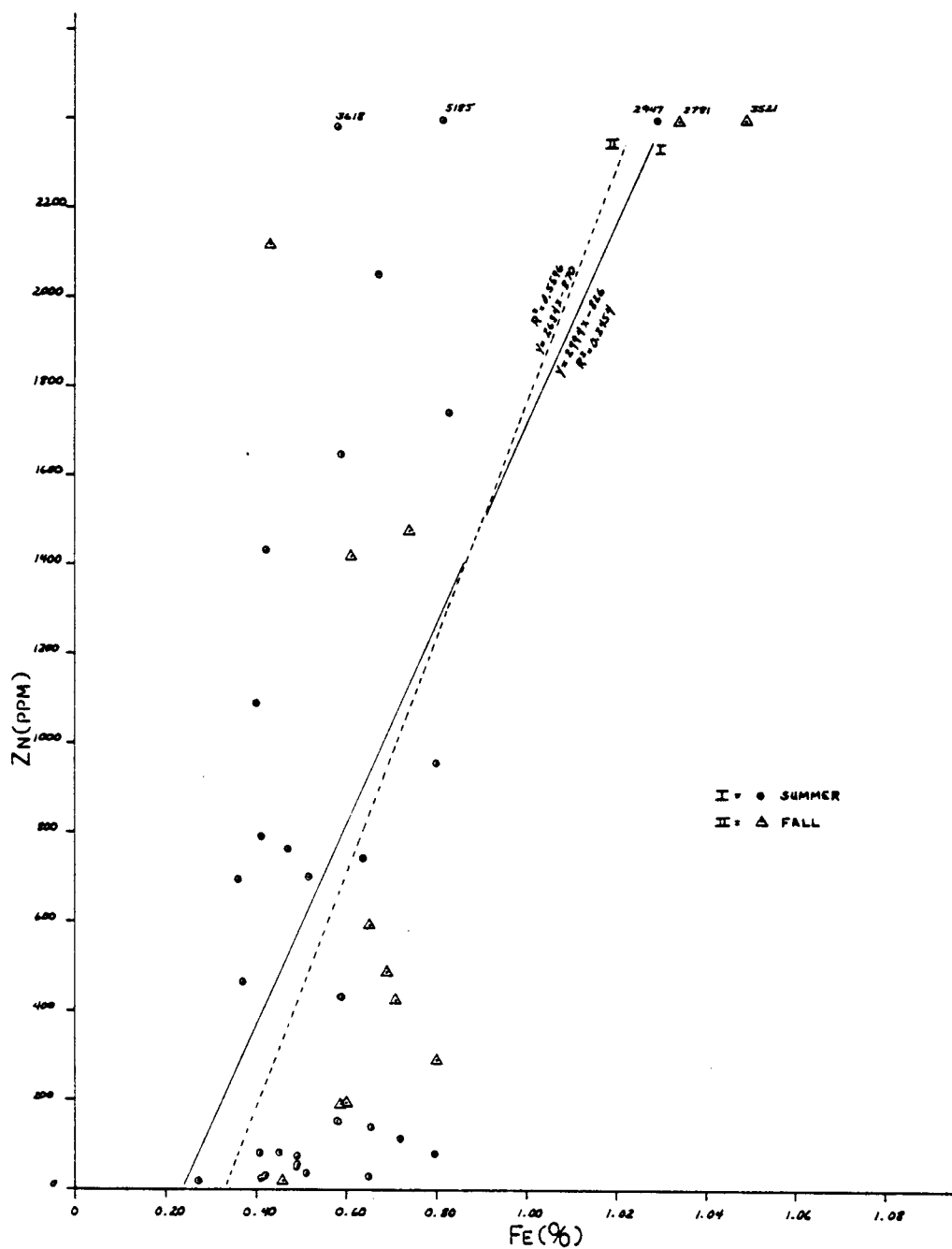


Figure 46. Scatter Plot of Zn versus Fe Concentration in Surficial Sediments During Cruise I and II

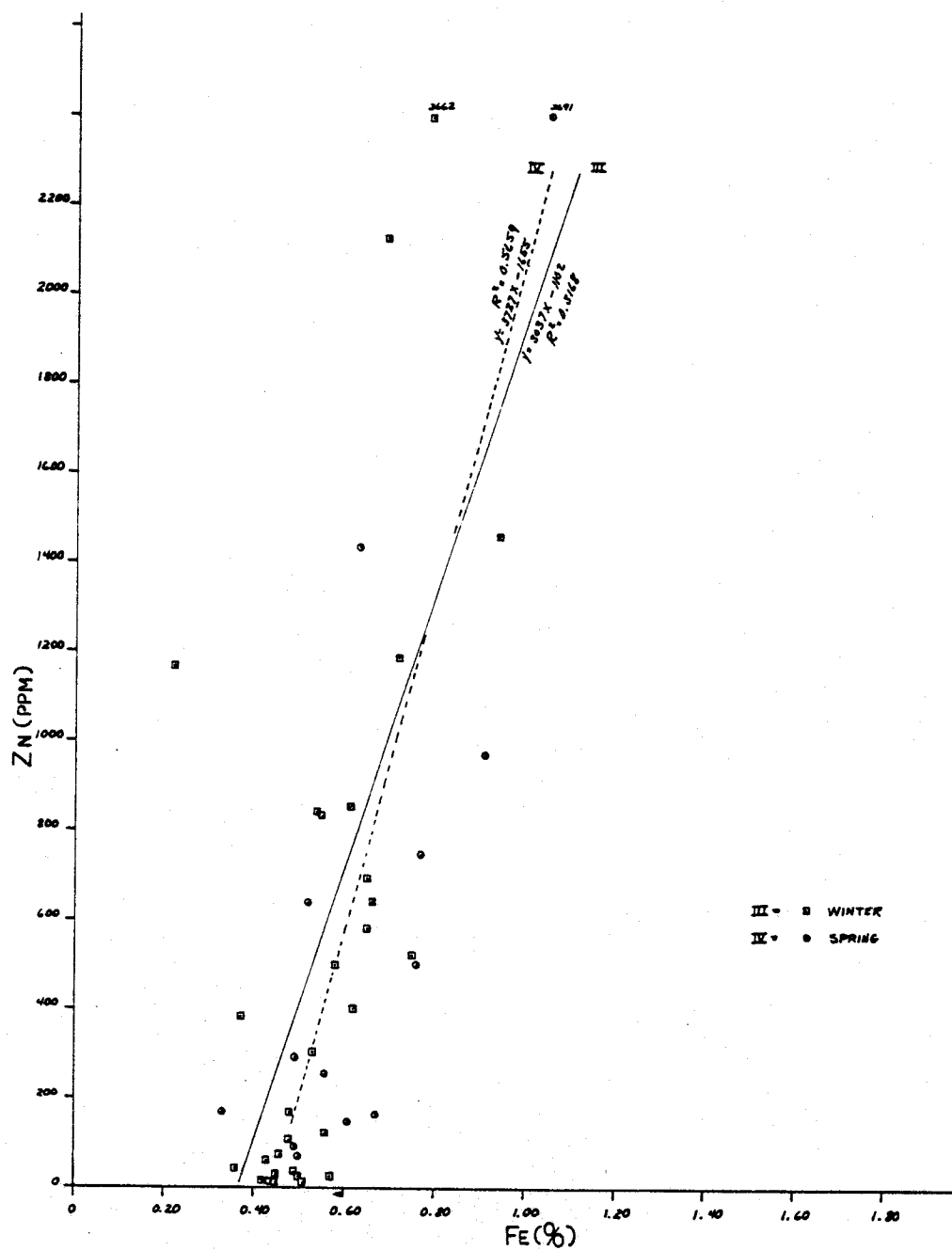


Figure 47. Scatter Plot of Zn versus Fe Concentration in Surficial Sediments During Cruise III and IV